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ALUMINIUM INTERACTION WITH ORGANIC MATTER AND FLUORIDE DURING SOIL DEVELOPMENT IN OXIDISED MINE WASTE

A thesis presented in partial fulfilment of the requirements for
the degree of Master of Science in Soil Science
Massey University

SHIVARAJ GURUNG

1994

ABSTRACT

Significant differences in plant growth response between unmodified waste rock (UWR) and modified (treated with lime and phosphate fertilizers) waste rock (MWR) with topsoil treatments during the first two years of a field trial conducted by Gregg & Stewart (1986; 1987) indicated that Al toxicity was affecting root growth in the UWR. By the end of three years of field trial there was no significant difference in dry matter yield between the MWR and UWR with topsoil treatments indicating possible amelioration of Al toxicity (Gregg et al., 1990). The objective of this study was to measure different forms of Al and F in the soil and waste rock at the end of the third year of field trial and to determine the mechanism of amelioration of Al toxicity in these soils.

Results of this study revealed that there was a significant 2-fold increase in organic-Al (Al-OM) at the UWR interface (B) compared with the waste rock at depth (C) by the end of three year period of soil development. Organic matter decomposition in the topsoil during three years and movement of the soluble organic ligands to UWR interface (B) resulted in conversion of phytotoxic soil solution Al into non-toxic Al-OM forms by complexation with organic ligands in leachates accumulated in the UWR interface.

Total soluble F was consistently high in the UWR profile with a mean value ranging from 1.0 to 1.9 $\mu g\ g^{-1}$. Liming has reduced the F level to 0.3-0.4 $\mu g\ g^{-1}$ in the MWR interface (B) and 0.4-0.5 $\mu g\ g^{-1}$ in the topsoil (A). The waste rock at depth (C) had mean

F values in the range 1.2-1.9 μg g^{-1}. High levels of F in the waste rocks could have also ameliorated Al toxicity in the UWR by formation of non-phytotoxic soluble AlF complexes. This was considered to be another possible reason for no significant differences in the pasture yields between UWR and MWR plots at the end of the third year of trial.

The mean soil pH(H_2O) for the UWR was 5.1 and liming has raised it by about 1 unit in the MWR. The corresponding pH(0.01 M $CaCl_2$) values were 0.4-0.8 units less than the pH in water. The 0.02 M $CaCl_2$-extractable solution Al (Al-Ca) and 1 M KCl-extractable exchangeable + solution Al (Al-K) have remained high in UWR soil solution irrespective of different depths of topsoil treatments. The Al-Ca and Al-K ranged from 16.7 to 20.5 μg g^{-1} and 261 to 339 μg g^{-1} respectively in the UWR interface (B). The Al-Ca and Al-K in waste rock at depth (C) remained at 16.8-22.9 μg g^{-1} and 238-369 μg g^{-1} respectively. Modifications have lowered both Al-Ca and Al-K to 0.8-2.7 μg g^{-1} and 35-66 μg g^{-1} respectively in the MWR interface (B). Topsoil Al-Ca and Al-K were not significantly different between UWR and MWR and the values for these two forms of Al ranged from 0.6 to 6.0 μg g^{-1} and 32-87 μg g^{-1} respectively at the end of the field trial. Normal plant growth response in the UWR in spite of high levels of Al-Ca and Al-K indicated that 0.02 M $CaCl_2$ and 1 M KCl extractants are not good indicators of phytotoxicity as reported in literature because these extractants may be extracting a substantial proportion of non-phytotoxic species of Al.

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To Kesherie & Ishka

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CHAPTER I

1. INTRODUCTION

1.1 Background

The Waihi Gold Mining Company is currently mining gold and silver from the Martha Hill Deposit. When mining is completed it is estimated that approximately 22 million tonnes of mine waste and 11 million tonnes of tailings from ore processing will be created from the site. The Waihi Gold Mining Company was required to submit an acceptable plan for the disposal and rehabilitation of the mine waste materials. Thus a conceptual mine plan incorporated the disposal of mine waste materials at the Baxter Road location and progressive restoration of the disposal area to the original land use i.e. pasture farming was developed.

Glasshouse and field trials were required to assess the suitability of the mine waste materials as plant growth media. Glasshouse pot trials carried out by Widdowson et al. (1984) characterised the oxidised mine waste material as having good potential as a plant growth medium. Table 1.1 summarises relevant chemical and physical properties of the oxidised waste material from their data. Their studies showed that the oxidised waste material contained toxic levels of exchangeable Al (8.5 me.%) and was deficient in some major (N, P & Ca) and micro-nutrients (Fe, Cu, Zn). Thus high levels of Al in the oxidised waste was indicated as one of the possible constraints to plant growth. However, the waste material supported good plant growth after adequate chemical modifications

Table 1.1. Selected chemical and physical properties of the oxidised waste rock and topsoil (Martha Hill, Waihi).

CHEMICAL PROPERTIES	Oxidised Waste	Topsoil
pH(H2O), 1:2.5 soil to water	5.2	5.3
CEC, me.%	14.4	29.0
BS, %	26.0	25.0
Ca, me.%	0.2	2.9
Mg, me.%	3.0	0.7
K, me.%	0.4	0.3
Al (KCl-extractable), me.%	**8.5**	**2.1**
P (Olsen), ppm	0.1	9.0
S (CaHPO4-extractable), ppm	35.0	22.0
P-retention, %	28.0	91.0
Organic Matter, %	0.2	10.4

PHYSICAL PROPERTIES	Oxidised Waste	Topsoil
Bulk density, (T/cu.m)	1.4	0.6
Total porosity, %	47.5	79.3
Macroporosity, %	17.0	6.5
Water content, %	33.4	
Plant Available Water, %	27.6	38.3
% < 2 mm fraction	71.0	
Texture	gritty clay loam	silt loam

Data from Widdowson et al. (1984) and
Gregg & Stewart (1986)

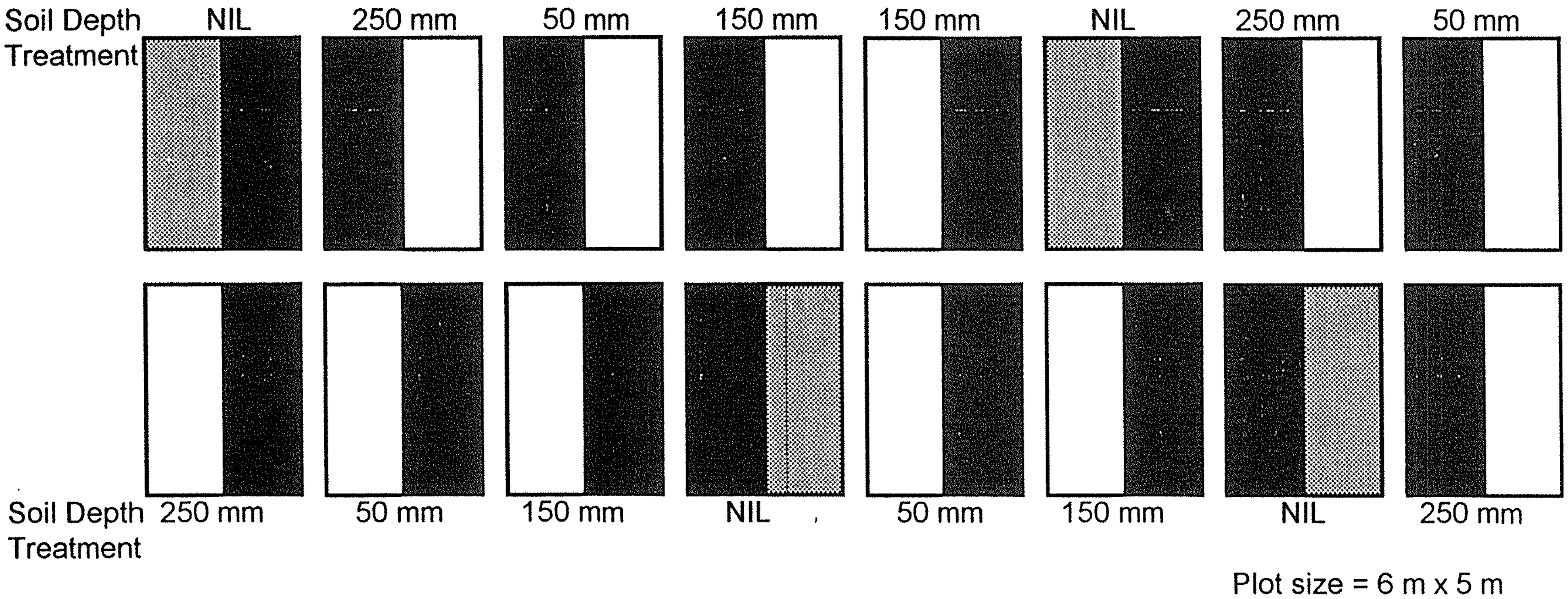
were made (Widdowson et al., 1984; Gregg et al., 1988). The oxidised waste material was also prone to compaction and low aeration during rehabilitation. This finding was confirmed by Horne et al. (1990).

One of the recommendations made by Widdowson et al. (1984) was that it was necessary to carry out field trials to determine the depth of soil cover required for optimum plant growth on oxidised waste rock. Further work was also suggested for studying the inhibitory effects of the mine waste materials on plant growth.

Based on their recommendations and in consultation with the Waihi Gold Mining Company, a three year field trial (1985-88) to assess the plant growth medium potential of the oxidised mine waste was carried out at the Martha Hill site (Gregg & Stewart, 1990). The major treatment studied was topsoil depth requirement for restoration of the oxidised mine waste. The plot design and treatments used are shown in Figure 1.1. The opportunity was also taken to examine the effect of modifying the oxidised waste with lime (6T/ha) and potassic superphosphate (100 kgP/ha) prior to topsoil placement (modified plots) as this was a viable rehabilitation option.

Results from the field trial (Gregg et al., 1990) showed that dry matter yield on the modified waste rock (MWR) plots was significantly (almost 2-fold) higher when compared with unmodified waste rock (UWR) plots during the first year (1985-86) of pasture growth. However at the end of the three year trial period (1985-88) there was no difference in yield between the UWR and

Figure 1.1 Martha Hill trial site (adapted from Gregg & Stewart, 1986)



WASTE ROCK MODIFICATION

Modified waste rock (MWR) ■ **(6T Lime + 100 kgP)/ha. incorporated to a depth of 150 mm**

Modified waste rock (MWR) ▒ **(6T Lime + 50 kgP)/ha. incorporated to a depth of 150 mm**

Unmodified waste rock (UWR) □ **No lime or phosphate applied**

*** Urea @ 30 kgN/ha was applied to all plots during pasture growth and after each harvest**

MWR plots, irrespective of topsoil treatments. Moreover, relative yield on the MWR with nil soil treatment was comparatively high throughout the trial period. Thus, although adequate lime application could have ameliorated Al toxicity in the MWR interface (B), some other agents must be responsible for inactivating reactive Al at the UWR interface (B). Speculative possibilities were that the good plant growth response on soils placed over UWR was either due to a "swamping" effect of P from the phosphatic fertilizer or that the Al may have been detoxified by organic and other leachates produced from topsoil placed over UWR.

Wright (1991) attempted to identify possible mechanisms of conversion of toxic Al in the UWR into nontoxic forms. He observed that there was no significant difference in KCl and $CuCl_2$-extractable Al in the shallow and deep samples of the waste rock and concluded that Al may not be toxic component. Mechanisms such as polymerisation of Al-hydroxides, Al binding by organic matter and complexing with available P to form Al-phosphate complexes were likely possibilities suggested by him. However, his findings were inconclusive because of the limitations of data from KCl and $CuCl_2$-extractable Al which measures exchangeable and organic bound Al, respectively.

Recent studies have shown that F in soil solution can exert a strong influence in detoxifying Al (Manoharan et al., 1994). The suspected high concentration of F in the mine waste could have detoxified Al in the UWR at Martha Hill site, thus giving another explanation for obtaining no differences in yield between UWR and MWR in the third year of plant growth.

1.2 Objective

The objective of this study was to investigate possible interactions of Al with organic matter and F during soil development in the oxidised mine waste. Quantitative determination of the different fractions of Al present in the soil extracts and F concentrations were therefore carried out to investigate if Al-organic matter or Al-F complexing was responsible for decreasing the toxic effects of Al in the unmodified waste rock (UWR) plots.

CHAPTER II

2. LITERATURE REVIEW

2.1 Introduction

Aluminium toxicity is a worldwide agricultural problem in acidic soils and it is increasing with heavy use of chemical fertilizers without adequate liming practices (Foy, 1971; Edmeades et al., 1983; Bache, 1985; Wright, 1989; Mackay, 1991). Low pH, predominant kinds of clay minerals, cation exchange capacity of the soils, salt concentrations and organic matter content are some of the recognised factors that influence Al concentration in soil solution and its subsequent impact on plant growth. Several studies have been done on toxic effects of Al on plant growth in soil media (Adams & Lund, 1966; Webber et al., 1982; Edmeades, 1985; Wright & Wright, 1987; Hern et al., 1988) but very few relate directly to mine waste materials.

The reactive Al pool in acid soils would ideally include soluble monomeric and total exchangeable Al, Al-hydroxides, Al in octahedral clays, organic-Al, Al-hydroxide-organic matter complexes (Juo & Kamprath, 1979). Methods to describe the Al status of the soil quantitatively however, are often based on limited knowledge of soil Al chemistry (Bache & Sharp, 1976). For example, current methods to quantify toxic levels of Al in soil solution do not discretely identify species involved and the extraction methods so employed are often open to question as to what Al is being extracted.

Lime in various forms, gypsum and large quantities of organic matter are commonly used to ameliorate Al toxicity in acidic soils. Whether such practices directly detoxify Al or activate other factors conducive to plant growth is yet to be understood fully. Several studies show that organic matter in the topsoil removes much of the Al from the soil solution pool, thereby reducing the concentration of toxic Al species (Mortensen, 1963; Hoyt & Turner, 1975; Young & Bache, 1985; Evans, 1986; Hargrove, 1986; Tan & Binger, 1986; Hern et al., 1988; Shuk-Ching & McColl, 1990). Understanding the cause and effects of toxic levels of Al and its implications to reclamation and restoration of mine waste materials as suitable plant growth media is an important consideration in mine environmental planning. The following literature review highlights some of the issues relevant to this study.

2.2 Soil Al Chemistry

Aluminium in soil solution occurs in a variety of forms that are controlled primarily by pH, soil parent materials and land use practices. In acidic soils of $pH \leq 5.5$, monomeric Al^{3+} is the predominant species present with lesser amounts of $Al(OH)^{2+}$ and $Al(OH)_2^+$ (Black, 1982; Nordstrom & May, (1989); Mackay et al., 1991). Figure 2.2 shows the distribution of monomeric forms of Al present at relative activities over normal soil pH range (Nordstrom & May, 1989). As the solution pH increases, these species continuously hydrolyse to form series of soluble Al-hydroxy compounds up to pH 7.5. A further increase in pH leads to formation of precipitates of insoluble Al-hydroxides until at $pH \geq 7.5$ soluble aluminate complexes are formed (Bache & Sharp,

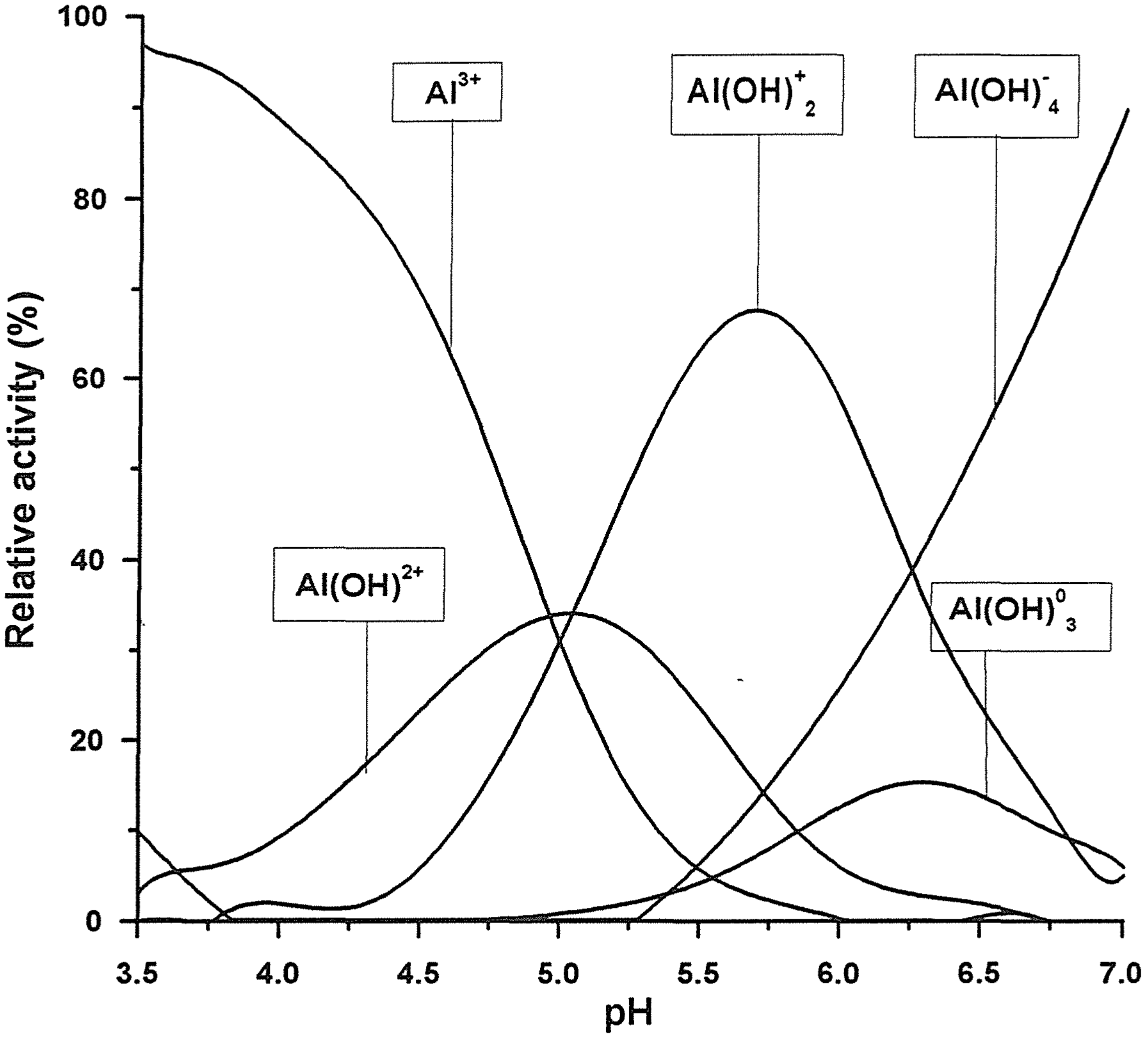


Figure 2.2 Relative distribution of Al^{3+} and mononuclear hydroxy-Al species as function of pH. The activities are in the absence of Al-complexing ligands and polynuclear Al species (after Nordstrom & May, 1989).

1976). The following equation summarized from McLaren & Cameron (1990) shows the likely generalised hydrolysis process taking place with increasing pH.

$$Al^{3+} + nH_2O <================> Al(OH)_n^{(3-n)+} + nH^+$$

Where n = atomic charge.
At elevated OH:Al ratios in soil solution, polynuclear hydroxy-Al complexes form. In the presence of Fe, Al is likely to form bidentate and polydendate metal complexes.

Both organic and inorganic ligands are likely to be complexed with soluble forms of Al. Organic ligands like ketonic functional groups and weak organic acids such as fulvic acid strongly complex with Al and mobilize it at near neutral pH (Young & Bache, 1985; Hargrove, 1986). Inositol hexaphosphate (phytic acid) is extremely stable in soil solution and forms insoluble salts with Fe and Al (McLaren & Cameron, 1990). Inorganic ligands such as SiO_4^+, SO_4^{2-} and F^- are known to form stable monomeric complexes with Al (Wright, 1989).

Aluminium complexation with applied fertilizer P has been attributed to P-fixation by Al (Wild, 1953; McLaren & Cameron, 1990). In acid soils, P ions can react with soluble Fe and Al to form extremely insoluble and plant unavailable precipitates of various Fe and Al phosphates. At sufficient concentrations of insoluble Al-hydroxy compounds, the precipitates of Al and Si lead to the formation of allophane (Parfitt & Saigusa, 1985).

Soluble monomeric Al ions freely bond through oxygen atoms to form variety of functional groups in soil solution. Indeed, Al bonding is central to soil acidity and nutrient deficiencies (Jackson, 1963). Phosphate and SO_4^- ions are chemisorbed in Al-hydroxy structures through substitution of -OH functional groups, a major mechanism for fixing of P in soils. Bache (1964) showed that crystalline Al-hydroxides absorbed 20 times less P than amount sorbed by non-crystalline form.

2.3 Al Toxicity in Acid Soils

Aluminium toxicity is often associated with acid soils and much research has been done to quantify toxicity levels detrimental to plant growth (Edmeades, 1985; Wright & Wright, 1987; Wright, 1989; Wright et al., 1989). In New Zealand, most hill country soils are acidic and hence invariably suffers from various levels of infertility related to Al toxicity. Considerable evidence suggests that plant growth is related to Al concentration levels in the soil solution (Webber et al., 1982; Tan & Binger, 1986; Wright & Wright, 1987; Mackay et al., 1991).

Typical Al toxicity symptoms in plant shoots resemble that of P deficiency in which chlorosis of the younger leaves and scorching of older leaves ultimately lead to premature shedding. Plant roots are the most seriously affected. Roots in seedlings are frequently stunted with many short laterals (McLaren & Cameron, 1990). Curling and rolling of leaves similar to those induced by Ca deficiency and collapse of the petioles are also typical Al toxicity symptoms (Foy, 1971).

Field and glasshouse trials on the suitability of plant growth media on gold and silver mining waste (Gregg & Stewart, 1987) showed that abnormal root growth symptoms of maize was typical of Al toxicity in unlimed mine waste. The root growth restrictions were attributed to P-deficiency and Al toxicity. They found that root penetration was confined to 15 cm depth but this was increased by liming to 30 cm. Pot trial on grass and white clover (Gregg & Stewart, 1987) grown on oxidised mine waste showed that lime and P increased dry matter production but the major cause of reduced clover growth on the unmodified waste rock was Al toxicity as exhibited from typical abnormal root growth symptoms. Research on reclaimed strongly acidic minespoils by Dancer & Jansen (1987) showed that corn growth without topsoil contained low concentrations of P (≤ 2.5 g kg^{-1}) and Ca (≤ 40 g kg^{-1}) suggesting Ca and P absorption by plant roots were inhibited by Al toxicity.

Pasture species and varieties differ in their tolerances to varying levels of Al. Limited glasshouse studies on white clover species (Edmeades et al., 1983 and Edmeades, 1985) showed that lotus (lotus pedunculatus) was better adapted than white clover (Trifolium repens) at the same concentration levels of Al. The trial also showed that Al toxicity restricted nodulation and reduced growth in white clover. Williams et al. (1981) have reported that there was an improved performance of the white clover Tahora cultivar relative to white clover Huia cultivar grown on acid hill country soils. Keltjens & van Ulden (1987) reported a negative effect of Al on nitrate uptake in sorghum cultivars. They showed that toxic levels of Al reduced internal concentrations of major nutrient cations and resulted in Al-induced inhibition of nitrate reductase activity (NRA) in sorghum species. Another glasshouse study by Hume et al. (1988) showed that white clover pasture was affected by as little as 3.3 μg g^{-1} of 0.02 M $CaCl_2$-extractable Al in seven strongly acidic hill country topsoils and subsoils (yellow-brown earth, YBE) of North Island, New Zealand.

At low pH, toxic levels of Al inhibit plant growth and root development in plants such as clover, cotton and wheat cultivars (Foy, 1971). Rooting systems restricted to the top few centimetres of a soil profile can make plants vulnerable to droughts and nutrient deficiencies in very acid soils with toxic levels of Al at depth. Toxic levels of Al in soil are found to be both soil and plant specific (Adams & Lund, 1966; Hoyt & Nyborg, 1972; Hume et al., 1988).

2.4 Methods of Determining Toxic Levels of Al

Several methods have been developed to measure toxic Al in soils and they include use of extractants such as 1 M KCl (Blackmore et al., 1987), 0.01 M $CaCl_2$ (Clarke, 1965), 0.02 M $CaCl_2$ (Hoyt & Nyborg, 1972; Close & Powell, 1989) and soil solution Al (Adams & Lund, 1966). These methods have often been modified (Hoyt & Webber, 1974; Jarvis, 1986) to suit extraction for a particular soil type.

Toxic levels of Al in soils are determined by using soil chemical properties such as pH, exchangeable Al, soluble Al, Al saturation and soil solution Al (Cameron et al., 1986). However, these methods have not yet been universally calibrated to cover a wide range of soil types and plant species. One of the major concerns in measuring toxic Al is how representative soil extractants are of field conditions (Jarvis, 1986). Aluminium concentration in 0.01 M $CaCl_2$ extracts has been considered by some to be comparable to that found in solution under field condition. The fact that there is a sharp decrease in mobile 0.01 M $CaCl_2$-extractable Al in very narrow pH range for a number of soil types has been taken to suggest that this extractant may be appropriate for identifying toxic levels of Al in soils (Jarvis, 1986).

Aluminium extracted with 0.5 M $CuCl_2$ and 0.33 M $LaCl_3$-solutions is mainly attributed to organic-Al plus other Al-hydroxy complexes. 1M KCl and 0.02 M $CaCl_2$-extractable Al is not an accurate measure of toxic levels of soluble Al in soil solution since these extractants also contain variable amounts of other species that may not be phytotoxic. The specific forms of phytotoxic Al extracted by these solutions cannot therefore be quantified.

In an experiment to measure toxic levels of monomeric and total Al in selected New Zealand soils, Percival et al. (1994) showed that < 1% and < 20% of monomeric Al was present in 1M KCl and 0.02 M $CaCl_2$ extractions respectively. The rest of the Al was either bound to organic complexes or in polymeric forms. The proportion of monomeric Al in soil solution was generally < 10% of the total Al extracted. With such discrepancies, Percival et al. (1994) speculated that soil solution Al levels in soils bear little relationship to 1 M KCl and 0.02 M $CaCl_2$-extractable Al. However, Hoyt & Webber (1974) found high correlation of 0.01 M and 0.02 M $CaCl_2$-extractable Al with % yield in barley. They found that 0.02 M $CaCl_2$-

extractable soluble Al was better related to crop data than 1 M KCl-extractable exchangeable Al.

There also seem to be a wide variation in Al determination techniques used. Hsu (1963) developed the Aluminon method for determining 0.01 M $CaCl_2$-extractable Al, and this method has been modified by Hoyt and Nyborg (1972). Quantitative determination of Al has been done by both pyrocatechol violet (Bromfield, 1987) and atomic absorbtion spectrophotometry (Blackmore et al., 1987) methods. Kennedy & Powell (1986) found that Al determination by using chrome azurol S (CAS) method is appropriate for rapid semi-quantitative analysis of labile Al in acid soils.

Naidu (1985) compared the effect of different salt concentrations on Al extractions and showed that there was significant variation in the amount of Al extracted by different salts. There were also variations in the amounts of Al in the salt extracts determined by Oxine (Bache & Sharp, 1976), Aluminon (Hsu, 1963) and atomic absorbtion spectrophotometry (Blackmore et al., 1987) methods. Accurate determination of Al is often hindered by interference of other soluble cations and anion ligands present in the soil solution although in the case of the Aluminon method, Page & Bingham (1962) showed that it can be suitably eliminated by an ion exchange column. Interference by Ca^{2+} at high Al levels cause Ca^{2+} turbidity and at $P > 50$ ppm and $Si^{4+} > 10$ ppm, colour development is depressed at low Al concentrations in Aluminon method (Frink & Peech, 1962). The use of ion exchange colloids to mask interfering ions such as P and Si was found to be selective and does not prevent other cation interference (Hsu, 1963).

Since there is no single Al determination method that satisfies the wide variation in soil types and plant species, the current methods of extraction and detection of Al in soils can only be used as rough diagnostic indicator of Al toxicity in soils. Parfitt et al. (1994) showed that Al levels were highly variable under different land use and management practices. Aluminium concentration was found to be soil specific and the level measured in the soil extracts and solutions is dependent upon sampling parameters, topographic expression and environmental conditions. In New Zealand, 0.02 M $CaCl_2$-extractable soluble monomeric Al (Hoyt & Nyborg, 1972) is currently used as an estimate for phytotoxic Al levels in acid soils. Glasshouse experiments by Edmeades (1985) showed that 0.02 M $CaCl_2$-extractable Al can be closely correlated with clover growth response and yield in New Zealand soils. Short-term bioassay techniques that measure root development to predict Al toxicity of the soil solutions has been suggested by Wright et al. (1989).

Aluminium toxicity in acid soils is a major worldwide problem and it is becoming increasingly important that standard methods of measuring phytotoxic Al be developed. The salts currently used to extract Al do not duplicate the actual ionic strength of the soil solution in field conditions. Thus the use of $CaCl_2$ and KCl solutions as standard extractants for extracting Al from soils should be used with caution because these extractants also extract both toxic and non-toxic forms of Al.

2.5 Critical Phytotoxic Levels of Al

Critical toxic levels of Al in soil solution depend on pH, soil type, plant species, soil organic matter, P status, salt concentration and other interfering ions present (Adams & Lund, 1966; Evans, 1986). Glasshouse trials by Edmeades et al. (1983) and Edmeades (1985) showed that Al toxicity limited root growth of white clover at pH(KCl) $\leq$ 4.1 and 1 M KCl-extractable exchangeable Al > 90-180 $\mu g\ g^{-1}$ in acidic steepland yellow-brown earth (YBE) and brown granular clay (BGC) under pasture in New Zealand. Clover growth was severely restricted with 0.02 M $CaCl_2$-extractable solution Al $\geq$ 3 $\mu g\ g^{-1}$. This corresponded to Al (activity) in soil solution $\geq$ 9 μM. A similar study by Wright & Wright (1987) on subterranean white clover in Appalachian soils (U.S.A) related critical Al toxicity in terms of Al saturation (exchangeable Al x 100 / CEC). They found that root growth and yield in unlimed acid soil with Al (saturation) > 10% was < 70% compared to that of limed soil and that soil solution Al activity > 3 μM inhibited clover root growth. Blamey et al. (1987) observed similar range of Al toxicity affecting clover growth in soil solution culture. They found that clover growth was significantly depressed at solution Al $\geq$ 24 μM and nodulation was significantly decreased at solution Al $\geq$ 6 μM. They also found that in legume-rhizobium symbiosis, nodulation was depressed at 25 μM solution Al but free living rhizobium tolerated up to 100 μM Al in the solution culture. In an experiment on the effects of Al^{3+} on cultivars of white clover grown in flowing solution culture, visual symptoms of P and N deficiencies were observed at 25 and 50 μM of solution Al respectively (Jarvis & Hatch, 1987).

Mackay et al. (1991) compared Al tolerance of forage species in acidic Wainui silt loam (New Zealand) and showed that at 1.35 me.% (122 $\mu g\ g^{-1}$) exchangeable Al, there was dominance of grass growth over leguminous species. In glasshouse soil solution culture experiment, Hume et al. (1988) found that 0.02 M $CaCl_2$-extractable soluble Al $\geq$ 3.3 μg g^{-1} severely depressed root growth in white clover. He also showed that Al determination by atomic absorbtion spectrophotometry (AAS) from the same extract gave a toxic soil solution Al of $\leq$ 5.1 μg g^{-1}. Other studies have also shown that there is a strong negative correlation between clover yield / root elongations and $CaCl_2$- extractable soluble Al (Webber et al., 1982; Hume et al., 1985). According to Close & Powell (1989), chrome azurol S (CAS) reactive 0.02 M $CaCl_2$-extractable Al $\leq$ 5.6 μg g^{-1} and $\leq$ 6.7 μg g^{-1} were critical threshold levels for 5 min. and 30 min. extraction time respectively. The critical level for 1 hour extraction time determined by AAS was $\leq$ 9.4 μg g^{-1}. Glasshouse experiments on steepland yellow-brown earth (YBE) and brown granular clay (BGC) soils showed that temperate legumes grown in these soils (Edmeades, 1985) plant growth was reduced by 50% at 10-15 μM soil solution Al and at solution Al 5-10 μM nodule formation was significantly reduced. At soil solution Al activity $\geq$ 1.5 μM cotton root penetration was restricted in the subsoil profile (Adams & Lund, 1966).

The degree to which Al toxicity symptoms are expressed by plants depends on a number of factors such as concentration and type of Al species present in soil solution, preferential adsorption on cation exchange sites, plant genotypes etc. (Wright & Wright, 1987). Therefore the reported critical levels of Al toxicity vary with soil chemical properties and the tolerance limits of the plant species concerned. Levels that are toxic in one soil may thus be well below or much higher than toxic levels in another soil.

It is interesting to note here that the determination of critical levels of Al have been mostly based on glasshouse experiments. In my view such experiments do not replicate field conditions where plant species, soil type, moisture content, physical properties, topographic expression and climatic variations may all be contributory factors in determining critical toxic levels of Al in the soil solutions. Thus a suitable standard method adaptable to field conditions needs to be developed for accurate determination of Al in soil solution which is independent of whether the soil is from the glasshouse or field.

2.6 Amelioration of Al Toxicity

Liming to raise pH is the widely accepted means of ameliorating Al in acid soils. Lime reduces $CaCl_2$ and KCl-extractable Al in acid soils and buffers titratable acidity (McLachlan, 1980). Ground limestone ($CaCO_3$) is the most commonly applied liming material. The effect of liming in locking up Al, especially in P deficient soils, has been suggested as an important control in the establishment of pastures (Fox et al., 1964). Mahilum et al.(1970) showed that the use of $CaSiO_3$ had a better effect than $CaCO_3$ in reducing exchangeable Al in aluminous soils under sugar cane crop. Gypsum applied on the soil surface has proven to be an effective ameliorant to Al phytotoxicity in the subsoil by increasing Ca^{2+} saturation and reducing Al^{3+} through complexation with SO_4^- released into the soil solution (Sumner, 1994). Phosphorus from applied phosphatic fertilizers readily complex with Al species in soils and thereby reduce Al toxicity in soil solution. The direct use of phosphatic fertilizers combined with lime initially raise pH and P levels and hence reduce soluble Al either by precipitation or by complexing with the P anions (Hume et al., 1988). Glasshouse trials (McLachlan, 1980) on lime and superphosphate application on acid soils show that the direct effect of these treatments was to increase exchangeable Ca^{2+} by displacing Al from cation exchange sites and precipitating it as Al-hydroxides and Al-phosphates respectively. Other Al complexing ligands such as organic ligands, SO_4^-, and F^- have also been infrequently used to detoxify Al in acidic soils. The use of green manures, municipal and dairy wastes also have potential to ameliorate Al toxicity in acidic soil. A study by Limpus et al. (1994) have shown that addition of sewage sludge to the mined materials resulted in beneficial increase in pH and organic matter and thereby help reduce toxic effects of Al in the soil solution.

Extractants such as 1 M KCl, 0.01 M $CaCl_2$, 0.5 M $CuCl_2$ and 0.33 M $LaCl_3$ have generally been used to predict plant response to liming and thereby indirectly, the reduction in Al toxicity due to liming (Wright, 1989). Lime requirement predicted by KCl-extractable Al is multiplied by a factor of 2 to compensate for the presence of other forms of Al not extracted with KCl salt which may still remain at phytotoxic levels in soil solution (Juo & Kamprath, 1979). Several authors suggest that 0.5 M $CuCl_2$ and 0.33 M $LaCl_3$ extractants are perhaps better predictors of lime requirements (Hsu, 1963; Juo & Kamprath, 1979; Kenneth & Kamprath, 1983; Jarvis, 1986) because they extract major portion of organic and polymeric Al-hydroxides responsible for buffering acid soils.

The frequency of liming depends on soil type, environmental conditions, lime residence time and the level of Al in the soil solution. Since very little downward movement of lime occurs below 30 cm depth (Bromfield et al., 1987), subsoil liming to ameliorate Al toxicity will be difficult to attain. In acid subsoils that contain low organic matter but high clay contents, lime requirements will be very high (Jackson, 1963).

Limited attempts to breed plant genotypes tolerant to Al have not been promising so far. Experimentation on Huia white clover species showed that the Al-tolerant gene was recessive and therefore not heritable to other population by hybridisation. However, selection of stronger Al-tolerant species of white clover within the population may be possible (Caradus et al., 1991). Direct selection of Al tolerant species hold some promise (Blamey et al., 1987) but this limits the varieties of pastures and crops that can be adapted to an acid soil environment with high levels of Al.

2.7 Al - Organic Matter Complexes

It has long been known that organic compounds are capable of forming complexes with metal ions such as Al^{3+} by surface adsorption, chelation and stoichiometric substitutions (Mortensen, 1963). Carboxylic and phenolic hydroxyl groups are considered to be the main organic ligands that complex with reactive Al (Aitken, 1992). The role of soil organic matter in ameliorating Al toxicity in acidic soils with $pH \leq 5.5$ has been well documented by numerous writers (Mortensen, 1963; Hoyt & Turner, 1975; Bache, 1985; Parfitt & Saigusa, 1985; Evans, 1986; Hargrove, 1986; Tan & Binger, 1986; Hern et al., 1988; Shuk-Ching & McColl, 1990). Aluminium-organic ligand interaction is thought to be responsible for effective immobilization of labile Al and hence lowering Al toxicity levels in soil solution (Shuk-Ching & McColl, 1990). Organic acids produced from decomposition of organic matter readily complex with Al in soil solution. Leachate from the organic matter consists of carboxylic acids similar to fulvic acids (Bache, 1985). The formation of Al-organic complexes in a near neutral environment (pH ≥ 5.5) is thought to be a possible mechanism for reducing Al toxicity in soils with adequate organic matter accumulation (Young & Bache, 1985). Experiments by Young & Bache (1985) have shown that organic bound Al in soils was linearly correlated with organic carbon and constitute about 20% of total Al in leachate and plant root exudate. In a study on acidic Queensland soils (Australia), Andrew et al. (1973) observed that formation of soluble organic-Al complexes constitute a major form of mobile Al in soil solution. The organic matter locks up or detoxifies the soil Al present in sufficient quantity. The mobilization of Al through soil profiles by organic ligand complexation may be the reason why initially forage species grow so well on freshly cleared forest soils but quickly lose fertility once Al levels and other toxic components are released into the surface soils as organic matter decomposes.

Tan & Binger (1986) have demonstrated that Al can move freely within the soil profile when it is complexed with simple organic ligands. Toxic levels of Al not only depend on forms of plant available Al but also on the relative Al-bonding affinity of carrier organic ligands. Strongly binding organic ligands protect against entry of phytotoxic Al into the plant root systems. Organic ligands are likely agents detoxifying Al in acid soils (Young & Bache, 1985).

It is now generally accepted that organic matter supplemented the need for liming in acid soils and that organic complexing by species such as fulvic and humic acids are likely mechanisms for Al mobility in acid soils with high levels of soluble and exchangeable Al.

In glasshouse studies with corn plants, Tan & Binger (1986) found that the presence of humic acid helps chelate Al and thereby leaves P free for plant uptake. This suggests that addition of organic substances containing humic acid can help block soluble Al in soil solution to plant tolerable levels. A study on acid forest soils by Ares (1986) has shown that organic ligands play a dynamic, quantitatively important role in defining Al speciation. This indicates possible translocation of labile Al in soil by ligand formations. The exchange of Al by anionic ligands from carboxylic sites on organic matter was the most important factor controlling the relationship between pH and Al activity in acid soil solutions of pH $\leq$ 5.5 (Wright, 1989). A study on acidic permanent grassland soils, Jarvis (1986) observed that low cation exchange capacity (CEC) in which organic matter is a major contributor to exchange complex can retain considerable amount of Al as polymerised organic complexes. He concluded that much of the extractable Al in soils was associated with organic matter.

Hern et al. (1988) showed that organic ligands can have a marked effect on migration of Al-organic matter complexes and subsequent ionic reactions of Al within the soil exchange matrix. In the presence of strong ligands, the translocation of free Al^{3+} to mobile organic complexes leads to vacation of cation exchange sites for adsorption of other cations such as Ca^{2+} and Mg^{2+}. Compared with

Ca^{2+} and Mg^{2+}, Al^{3+} has a relatively large energy of adsorption and unless it is removed from the exchange sites by strong organic ligands, the soil system remains effectively acidic.

The effect of large amounts of added organic matter in acid soils on reducing exchangeable Al and increasing pH and thus crop yield is attributed to Al-organic matter complexation (Hoyt & Turner, 1975). However, the effects are only temporary and the fact that a large quantity of organic matter is involved in order to achieve this effect, liming is still favoured as the most viable option to reduce Al toxicity in acid soils.

2.8 Al-F Complexation in Soil Solution

Soil type, pH, Ca, P and Al contents are the predominant factors controlling F concentrations in soil solution (Pickering, 1985). The main contribution of F in the soils comes from soil parent materials containing minerals such as apatite, mica, tourmaline, hornblende etc. and from use of phosphatic fertilizers. Phosphatic fertilizers are a major source of F in soils. For example, an application of 38 kg P $ha^{-1}yr^{-1}$ (4 kg F $ha^{-1}yr^{-1}$, SSP with 1% F) raised the F content of a soil from 0.4 to 0.6 ppm in one year (Larsen & Widdowson, 1971). A study of a slightly acidic New Zealand soil under pasture by Manoharan et al. (1994) has shown that long-term application of soluble phosphatic fertilizers (SSP & DAP) has resulted in a significant increase in both Al and F levels in soil solution of surface soils.

Fluoride readily reacts with Al^{3+} to form Al-F complexes. MacLean et al. (1992) showed that inclusion of F in wheat growth medium reduced Al toxicity in the rhizosphere by reduction of Al through formation of non-phytotoxic Al-F complexes. He showed that 50-100 μM Al in the wheat growth solution media severely inhibited root growth but inclusion of the same amount of F ameliorated the effect. Fluoride at 200 μM in solution media completely reversed the inhibitory effects of 100 μM Al. At ratios of 1:1 and 1:2 Al to F, the likely complexes formed would be AlF^{2+} and AlF^{+}_{2}. Complexation was effectively complete at equimolar concentrations of Al and F. According to Pickering (1985), the possible Al:F complexes formed are AlF^{2+}, AlF_2^+ and AlF_3 depending on the concentration of each of the ions in soil solution.

A study of acid forest soils (Ares, 1986) has shown that in the presence of Si^{4+}, F ions readily coordinate with Al^{3+} and Si^{4+} to form hexafluoro complexes, $(AlF_6)^{3-}$ and $(SiF_6)^{2-}$, respectively (Black, 1982). Aluminium-F complexes are highly stable and monomeric species like Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ can readily react with F through favourable reaction kinetics (Ares, 1986). Such complexation reduces toxic levels of both elements in soil solution. Fluoride is adsorbed in the soil much like P and the amount available for complexing with Al depends on organic matter and allophanic clay content which readily adsorb F in their large pool of positive charge and even at neutral sites (Black, 1982).

Fluoride concentration in agricultural soils is typically 1-20 ppm and it is likely that much of it comes from application of phosphatic fertilizers (Bache, 1985). Literature values for total F contents in phosphatic fertilizers, soils and plant are $3x10^4$ ppm, $3x10^2$ ppm and 3 ppm respectively (Larsen & Widdowson, 1971; Black, 1982;). Surface soils contain ≤ 1 ppm total soluble F and 0.01 M $CaCl_2$ typically extracts 0.0-0.4 ppm F at pH 4.0-6.5 to up to 1.4 ppm at pH 6.5-8.0 (Pickering, 1985). Larsen & Widdowson (1971) measured 0.01 M $CaCl_2$-extractable total soluble F ≤ 0.2 ppm in acid soils with total soil F values of up to 20 ppm.

From the foregoing review, it is apparent that Al toxicity in acid soils is one of the major factors restricting plant growth. In most mining activities, the mine waste materials generated are invariably acidic in nature. Hence the pH environment is right for the solubility of Al and other phytotoxic metal ions. The restoration and rehabilitation of these mine waste materials to original state (pasture, in the case of Waihi) will thus require chemical modifications to ameliorate subsoil acidity and reduce toxic effects of metal ions and create physical environment that is conducive to plant growth. Climatic condition, landscape design and management practices are other parameters that need consideration for a successful restoration process. Organic ligands, F and other ligands present in the soil solution are likely complexing agents that can ameliorate Al phytotoxicity in acid soils.

CHAPTER III

3. MATERIALS AND METHODS

3.1 Soil Samples

Oxidised waste rock and topsoil samples collected at the end of the field trial period (1988) from Martha Hill site (Figure 1.1) were used in this study. Eighty soil samples from four replicate plots of unmodified waste rock (UWR), topsoil (TSU) on UWR, modified waste rock (MWR) and topsoil (TSM) on MWR were collected as described below:-

Control plot (No topsoil treatment)	2 depths (B, C) x 4 replicate (MWR) =8
50 mm topsoil plot	3 depths (A, B, C) x 4 replicate (UWR) = 12
	3 depths (A, B, C) x 4 replicate (MWR) = 12
150 mm topsoil plot	3 depths (A, B, C) x 4 replicate (UWR) = 12
	3 depths (A, B, C) x 4 replicate (MWR) = 12
250 mm topsoil plot	3 depths (A, B, C) x 4 replicate (UWR) = 12
	3 depths (A, B, C) x 4 replicate (MWR) = 12
	Total number of samples = 80

Figure 3.1 shows the approximate sample locations from which the above samples were collected. Samples were taken from topsoil interface (A), waste rock interface (B) and waste rock at depth ≥ 300 mm (C) from both UWR and MWR plots of nil, 50, 150, & 250 mm topsoil treatments. The interface locations were approximately 30-50 mm on either side of the topsoil/waste rock contact surface.

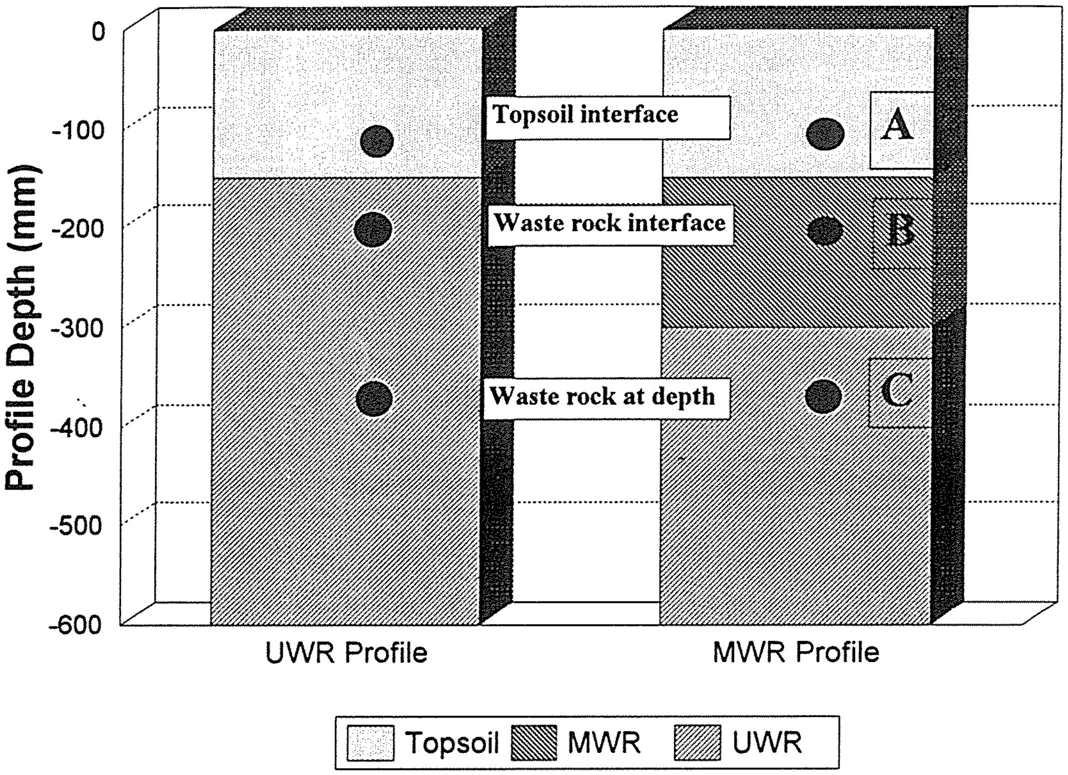


Figure 3.1 Approximate sample locations in modified (MWR) & unmodified (UWR) waste rock profiles.

3.2 Preparation of Soil Samples

Coned and quartered halves of the original samples, stored for 5 years (1988-1993), were ground and sieved through 2 mm mesh. The ground samples were again coned and quartered to make duplicates. Control samples were from an undisturbed reference site at Baxter Road, near Waihi.

3.3 Experimental Methods

The methods selected in this study were to determine quantitatively the different forms of Al present in the (MWR) and (UWR) waste rock interface (B), waste rock at depth (C) and in the overlying topsoil interface (A). Determination of total soluble F was also included in order to examine possible complexation of F with soluble Al in the waste rock and topsoil soil solution. All analytical measurements were done in duplicate.

3.3.1 Soil pH

pH(H_2O) and pH(0.01 M $CaCl_2$) were measured in 1:2.5 w/w soil to deionised water and 1 : 2.5 w/w soil to 0.01 M $CaCl_2$ ratios respectively (Blackmore et al., (1987). A standard PHM83 AUTOCAL pH METER was used to measure the pH at 20°C and 98.2% sensitivity. Manawatu #1 silt loam, an internal laboratory standard, was included.

3.3.2 0.02 M $CaCl_2$ Extractable Al (Al-Ca)

Ten grams of air-dried ($\leq$ 2 mm) soil was weighed into 50 ml polyethylene centrifuge tubes and 20 ml 0.02 M $CaCl_2$ was added to it. It was shaken on an end-over end shaker for 1 hour and centrifuged for 5 minutes @9000 rpm. The extracts were filtered through Whatman's filter paper no.42. Solution Al (Al-Ca) in the extract was determined by the Aluminon method as described by Hsu (1963).

In the Aluminon method, appropriate volumes (2 ml for soil $pH(H_2O) \leq 5.5$ and 5 ml for soil pH $\geq$ 5.5) of the extracts were transferred into 50 ml test tubes and 10 ml aluminon-acetate buffer was added to it. One ml of 0.5% ascorbic acid was also added to reduce interference by Fe-complexes. It was then diluted to 50 ml mark with 0.02 M $CaCl_2$ solution. The mixtures were shaken well and left overnight for colour development. Optical densities (absorbance) were measured on a Philips PU8620 Spectrophotometer @530 nm using a 1 cm cell after adjusting the absorbance of the reagent blank to zero. Absorbances were also measured on standard solutions containing reagent blank, 0.2, 0.4, 0.6, 0.8 ppm of Al made from 1000 μg/ml commercial stock solution diluted to 5 ppm. Aluminium concentrations of the soil extracts were read directly from a best fit regression curve of the Al (ppm) Vs absorbance standard graph.

3.3.3 1 M KCl Extractable Al (Al-K)

A modification of the method given by Blackmore (1987) was used to extract total exchangeable Al. Three grams of air-dried ($\leq$ 2 mm) soil was weighed into 50 ml polyethylene centrifuge tubes and 30 ml 1 M KCl was added. The mixture was shaken for 1 hour on an end-over-end shaker and centrifuged for 10 minutes @9000 rpm. The extract was filtered through Whatman's filter paper no.42 and Al concentration was determined by atomic absorbtion spectrophotometry (AAS) using N_2O / acetylene flame after calibrating the instrument with the standards.

In the AAS method, 5 ml of the extract was put into a 50 ml test tube and 5 ml 1 M KCl was added. The mixture was made up to 50 ml with deionised water. Standard solutions containing reagent blank, 5, 10, 20, 50 ppm of Al were prepared from 1000 μg/ml commercial stock solution diluted to 500 ppm.

Aluminium in the extracts was also determined by Aluminon method as described for Al-Ca.

3.3.4 0.5 M $CuCl_2$ Extractable Al (Al-Cu)

Organic + polymeric + exchangeable Al was determined by the method of Juo & Kamprath (1979). Three grams of air-dried ($\leq$ 2 mm) soil was weighed into 50 ml polyethylene centrifuge tubes and 30 ml of 0.5 M $CuCl_2$ was added. The mixture was shaken for 2 hours on an end-over-end shaker and centrifuged for 10 minutes @9000 rpm. The extract was filtered through Whatman's filter paper no.42. An attempt to measure Al in 0.5 M $CuCl_2$ extracts by the Aluminon method was unsuccessful due to rapid precipitation of Cu-hydroxide when pH was raised by the addition of 1 M NaOH.

The $CuCl_2$ solution was stable only at pH < 3.5 in the presence of Aluminon buffer. Therefore the Al in the $CuCl_2$ extracts was measured by AAS as described for Al-K.

3.3.5 0.01 M $CaCl_2$ Extractable Total Soluble F

Total soluble F in 0.01 M $CaCl_2$-extract was measured as described by Larsen & Widdowson (1971). Ten grams of air-dried ($\leq$ 0.40 mm) soil was weighed into 50 ml polyethylene centrifuge tubes and 30 ml of 0.01 M $CaCl_2$ added to it. The mixture was shaken overnight (16 hours) at 25°C on an end-over-end shaker and centrifuged for 5 minutes @9000 rpm. The extract was filtered through Whatman's filter paper no.42.

Five ml of the extract was mixed with an equal volume of TISAB (Total Ionic Strength Adjustment Buffer) of pH 5.24 in a 10 ml beaker. Total F concentration was obtained by measuring the stabilised millivolt reading on a F-ISE Fluoride Electrode Meter (Model 701A/digital IONALYSER) while being gently stirred by a magnetic stirrer. A best fit regression curve of a standard graph of F (ppm) Vs millivolts gave direct readings of F concentrations. Preparation of standard and TISAB were done as per Larsen & Widdowson (1971).

Total soluble F analysis was only done in replicate samples from UWR and MWR with 50 mm and 150 mm topsoil treatments.

CHAPTER IV

4. RESULTS AND DISCUSSION

4.1 Soil Chemical Properties

Tables 4.1, 4.2, and 4.3 list the mean plot-wise distribution of individual chemical properties of the modified (MWR) and unmodified (UWR) waste rock and topsoil treatments. Selected raw chemical data is presented in Appendix 1 and Appendix 2 compares the current data with that of earlier workers. Appendix 3 presents a comparison of the determination of 1 M KCl-extractable Al by atomic absorbtion spectrophotometry (AAS) and Aluminon methods.

4.1.1 Soil pH

The mean soil pH of the waste rock and topsoil are presented in Table 4.1. The soil pH(H_2O) varied from strongly acid in the unmodified waste rock (UWR) to near neutral in the modified waste rock (MWR) interface (B). The mean waste rock interface (B) pH(H_2O) values of the UWR and MWR plots were 5.0 and 6.1 respectively for all the topsoil treatments. The corresponding pH(0.01 M $CaCl_2$) values were 4.2 and 5.4 respectively for the UWR and MWR plots. The topsoil pH values ranged from 5.1 to 5.8 and 4.7 to 5.4 in H_2O and 0.01 M $CaCl_2$ respectively. Overall, there was very little difference in pH value between the waste rock at depth (C) and the UWR interface (B). The mean pH(H_2O) value of the UWR was 5.1 which was comparable to the waste rock pH value

Table 4.1. Mean pH in unmodified (UWR) and modified (MWR) waste rocks with topsoil treatments.

a

pH(H2O)	UNMODIFIED			MODIFIED		
Topsoil, mm	A	B	C	A	B	C
nil	n.d	n.d	n.d	n.d	5.8±0.2	5.0±0.1
50	5.4±0.1	5.0±0.1	5.2±0.2	5.8±0.1	6.1±0.6	5.0±0.1
150	5.3±0.2	4.9±0.1	5.2±0.1	5.3±0.3	6.1±0.7	5.1±0.2
250	5.3±0.1	5.0±0.1	5.0±0.0	5.4±0.2	6.1±0.7	5.2±0.1
Control	5.1±0.2	n.d	n.d	n.d	n.d	n.d

1 : 2.5 w/w soil to deionised water.

b

pH(CaCl2)	UNMODIFIED			MODIFIED		
Topsoil, mm	A	B	C	A	B	C
nil	n.d	n.d	n.d	n.d	5.3±0.2	4.1±0.1
50	5.0±0.1	4.3±0.1	4.3±0.2	5.4±0.1	5.4±0.7	4.1±0.1
150	4.7±0.3	4.2±0.1	4.1±0.1	4.8±0.3	5.5±0.9	4.1±0.1
250	4.8±0.1	4.2±0.0	4.2±0.0	5.0±0.2	5.5±0.9	4.2±0.1
Control	5.0±0.2	n.d	n.d	n.d	n.d	n.d

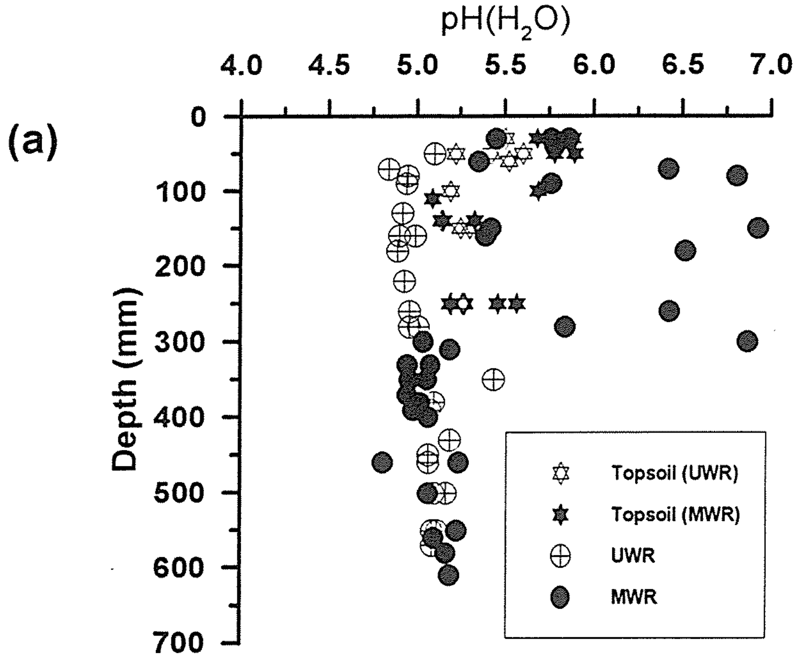
1: 2.5 w/w soil to 0.01 M CaCl2 solution.

Control= Undisturbed topsoil from Baxter Road location (Waihi)
n.d.= Not determined
A = Topsoil interface
B = Waste rock interface
C = Waste rock at depth

prior to commencement of the field trial (Table 1.1). The effect of addition of lime (@ 6T ha^{-1}, 1985) raised pH by about 1 unit at the MWR interface (B). Topsoil pH has remained constant at 5.3 for both the UWR and the MWR plots except for the 50 mm MWR plot where the pH is about 0.5 unit higher than the other plots probably due to some mixing with MWR interface soil. The topsoil values are about 0.5 and 0.7 units lower than that of the Autumn 1988 values reported by Gregg & Stewart (1986) for the UWR and the MWR plots respectively. As expected, measurement of pH in 0.01 M $CaCl_2$ shows that there is very similar trend to that of pH in water except the values were 0.4-0.8 unit lower than that of pH(H_2O).

The depth-wise variations of pH(H_2O) and pH(0.01 M $CaCl_2$) are shown in Figure 4.1. There was a wide variation in pH(H_2O) > 5.5 and pH($CaCl_2$) > 5.0 from the surface to a depth of about 300 mm in both MWR and UWR profiles. Below this depth there was no significant difference in pH between the UWR and MWR profiles. The mean pH(H_2O) below 300 mm profile depth remained at 5.1 irrespective of different depths of topsoil treatments.

The current pH(H_2O) data was comparable to the earlier data of Wright (1991) and Gregg & Stewart (1986) as shown in Appendix 2. Storage of the soil samples over a period of 5 years has not altered the soil pH.



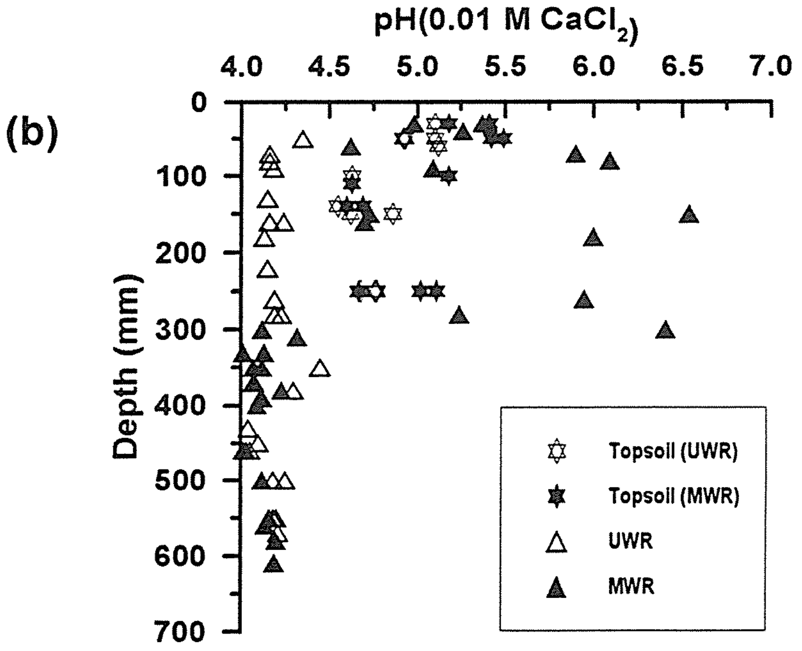


Figure 4.1 Soil pH variation with depth.

4.1.2. Soil Al

In this section, the following abbreviations are used :-

Al-Ca = 0.02 M $CaCl_2$-extractable Al.
Al-K = 1 M KCl-extractable Al.
Al-Cu = 0.5 M $CuCl_2$-extractable Al.
Al-OM = Al bound to organic ligands (Al-Cu minus Al-K).

There is little difference in Al-K values measured by AAS and Aluminon methods (Appendix 3) and therefore only the values obtained by AAS are reported in Table 4.2b. Results of the experiments showed that the UWR interface (B) and at depth (C) contained very high levels of Al-Ca and Al-K compared to MWR (Table 4.2). The Al-Ca and Al-K in UWR treatment at depth (C) were similar to those of MWR at depth (C). The mean Al-Ca value ranged from 16.7 to 20.5 $\mu g\ g^{-1}$ in the UWR interface (B). The corresponding values for the Al-K ranged from 261 to 339 $\mu g\ g^{-1}$. The Al-Ca and Al-K values for MWR interface (B) ranged from 0.8 to 2.7 $\mu g\ g^{-1}$ and 35-72 $\mu g\ g^{-1}$ respectively. The direct effect of lime and fertilizer applications had been to reduce both these forms of Al at the MWR interface (B). The mean Al-K in the topsoil ranged from 32 to 87 $\mu g\ g^{-1}$ where as soluble Al-Ca was in the range 0.6-6.0 $\mu g\ g^{-1}$. There was no difference in the Al-Ca and Al-K at depth (C) between UWR and MWR.

Al-Cu ranged from 467 to 549 $\mu g\ g^{-1}$ and 245 to 286 $\mu g\ g^{-1}$ in the MWR and UWR interfaces (B) respectively (Table 4.2c). The topsoil Al-Cu values ranged from 1039-1862 $\mu g\ g^{-1}$ and varied between the

Table 4.2. Distribution of mean Al values in unmodified (UWR) and modified (MWR) waste rock with topsoil treatments.

0.02M CaCl2-extractable Al (Al-Ca), µg/g

a	**Al-Ca**	UNMODIFIED			MODIFIED		
	Topsoil, mm	A	B	C	A	B	C
	nil	n.d	n.d	n.d	n.d	1.9±0.2	22.9±2.0
	50	1.5±0.3	19.2±2.9	18.4±1.8	0.6±0.1	1.1±0.3	19.8±1.6
	150	6.0±0.4	20.5±1.3	20.4±1.1	4.9±1.1	2.7±0.6	20.2±0.6
	250	1.9±0.8	16.7±0.4	16.8±0.5	3.0±1.8	0.8±0.1	17.1±0.4

1M KCl-extractable Al (Al-K), µg/g

b	**Al-K**	UNMODIFIED			MODIFIED		
	Topsoil, mm	A	B	C	A	B	C
	nil	n.d	n.d	n.d	n.d	36±7	319±7
	50	37±15	261±29	238±37	32±15	66±23	345±43
	150	87±27	339±66	334±24	66±32	72±36	369±26
	250	39±7	318±16	285±17	60±15	35±16	323±34

0.5M CuCl2-extractable Al (Al-Cu), µg/g

c	**Al-Cu**	UNMODIFIED			MODIFIED		
	Topsoil, mm	A	B	C	A	B	C
	nil	n.d	n.d	n.d	n.d	275±52	423±49
	50	1317±37	468±51	307±47	1039±16	269±23	427±32
	150	1453±15	509±104	442±17	1853±32	286±6	458±36
	250	1863±38	518±80	391±33	1262±15	245±19	437±47

Organic-Al, Al-OM = Al-Cu minus Al-K, µg/g

d	**Al-OM**	UNMODIFIED			MODIFIED		
	Topsoil, mm	A	B	C	A	B	C
	nil	n.d	n.d	n.d	n.d	239±58	104±43
	50	1280±37	206±63	70±55	1008±15	203±15	82±58
	150	1366±13	210±46	108±32	1787±34	214±33	89±17
	250	1823±38	200±86	107±30	1201±14	210±35	115±39

n.d.= Not determined

A= Topsoil interface B= Waste rock interface C= Waste rock at depth plots. This variation may have been due to localisation of the organic matter in the original topsoil, spatial variation in pasture compositions and mixing of topsoil with subsoil. For example McLaren & Cameron (1990) reported that organic matter accumulation in the top 20 cm soil was in the range 6000-8500 kg ha^{-1} for three years grass growth whereas the corresponding value for clover was only 2000 kg ha^{-1}.

The distribution of measured forms of Al was controlled by the soil pH as shown in Figure 4.2 and 4.3. Two distinct populations of data were observed. The data clustering at higher values of Al-Ca and Al-K were from the depths B and C of UWR and depth C of the MWR whereas the lower values represented the Al-Ca and Al-K in the interface B of MWR and in the topsoil of both UWR and MWR treatments (Figure 4.2). Distributions of Al-Ca and Al-K show a roughly negative exponential trend. While pH 5.5 seemed to be the upper limit of Al-Ca and Al-K forms present in the soil solution, no similar distinct boundary was observed for Al-Cu and Al-OM (Figure 4.3). The topsoil Al-Cu and Al-OM values are represented by the distinctly higher values. The variations in the Al-Cu values was greater for the topsoil than for the waste rock, showing spatial differences in the organic matter distribution and plant species variations within the plots. This trend also indicate that organic matter content is more important in determining Al-Cu content than pH. There was no difference in the level of Al-Cu and Al-OM at different depths of topsoil treatments.

Comparison of Al-K data with that of Wright (1991) and Gregg & Stewart (1986) showed that within limits of detection, the values

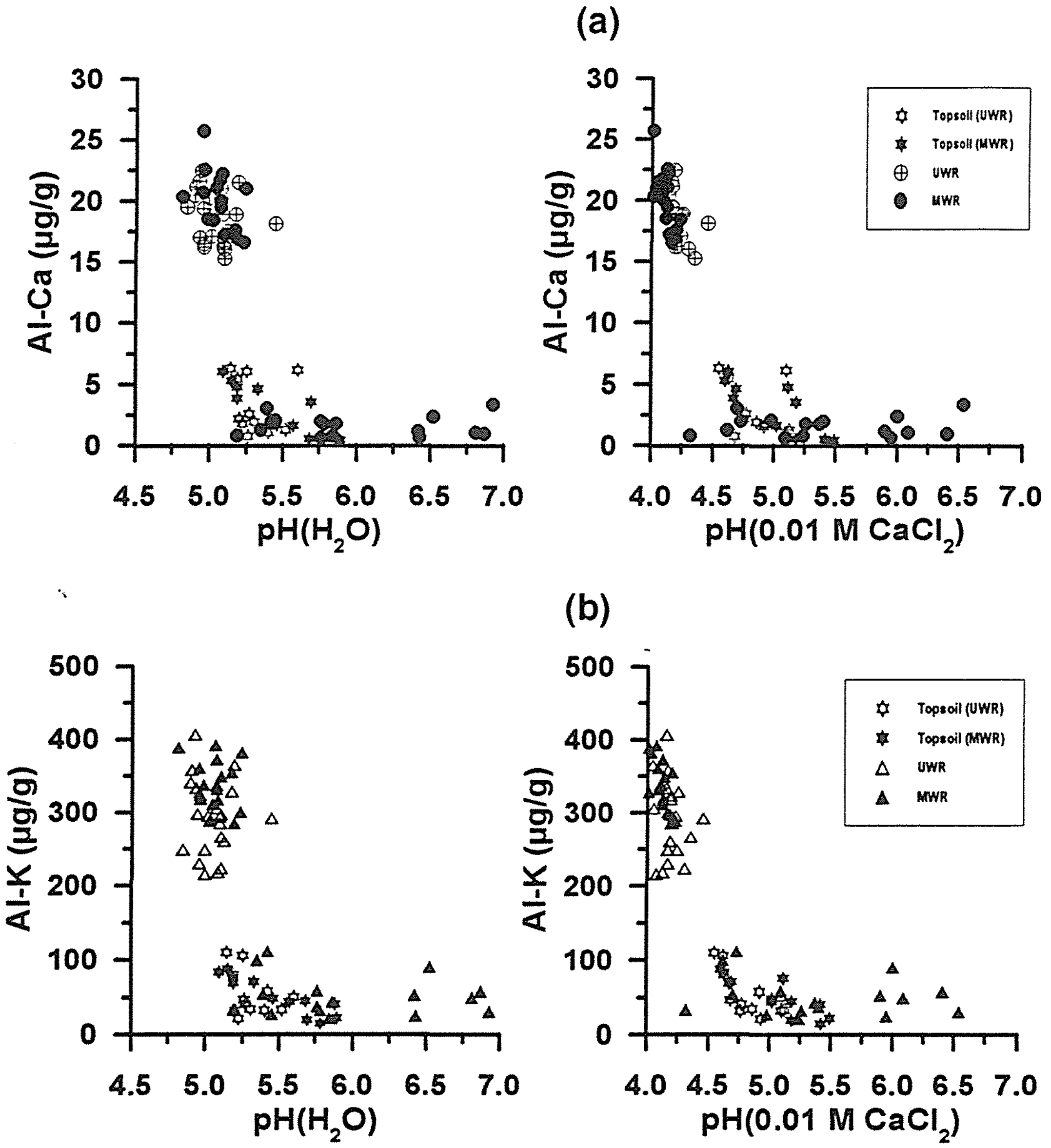


Figure 4.2 Variation of (a) Al-Ca and (b) Al-K with soil pH.

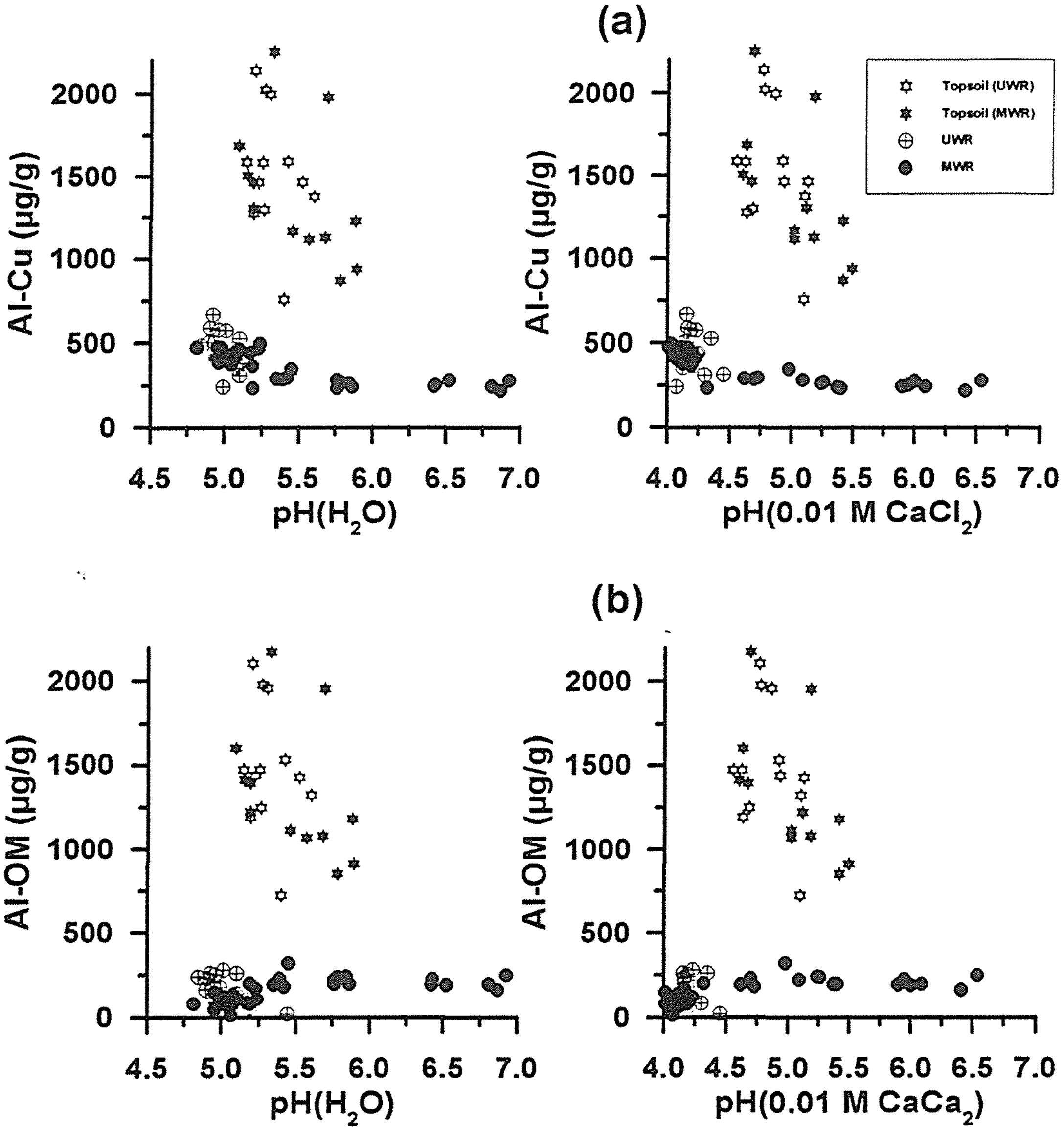


Figure 4.3 Variation of (a) Al-Cu and (b) Al-OM with soil pH.

were similar (Appendix 2). However there were differences in Al-Cu values between those of Wright (1991) and the values obtained in this study. The variation in the Al-Cu data could possibly be due to differences in sample preparation techniques. The current data for the 50 mm and 150 mm plots were from samples prepared from coarser fractions left by Wright (1991). It is possible that the finer fractions of soil samples analyzed by Wright could have contained higher amount of Al-Cu as shown by generally lower values of Al-Cu in this study.

The depth of topsoil treatments did not have any significant effect on all forms of Al extracted in this study.

4.1.3. Al - Organic Matter Interactions

The results of this experiment showed that there was evidence of complexing of reactive Al pool by organic ligands from accumulation, decomposition and subsequent leaching of soluble organic matter from the topsoil placed over the waste rock. The build up of Al-OM at the UWR interface (B) was significantly higher (LSD = 44, P = 0.05) than that of waste rock at depth (C) over the three year trial period (Table 4.2d, Figure 4.4). If we take the Al-OM value of the waste rock at depth (C) to be close to the original level of organically bound Al, then there is an indication that the Al-OM at the waste rock interface (B) had a significant 2-fold increase by the end of the three year trial period (Figure 4.4). Prior to the restoration of the waste rock, Al-OM value at the waste rock interface (B) would be the same as that of waste rock at depth (C) which had an organic matter content as low as 0.2% (Table 1.1).

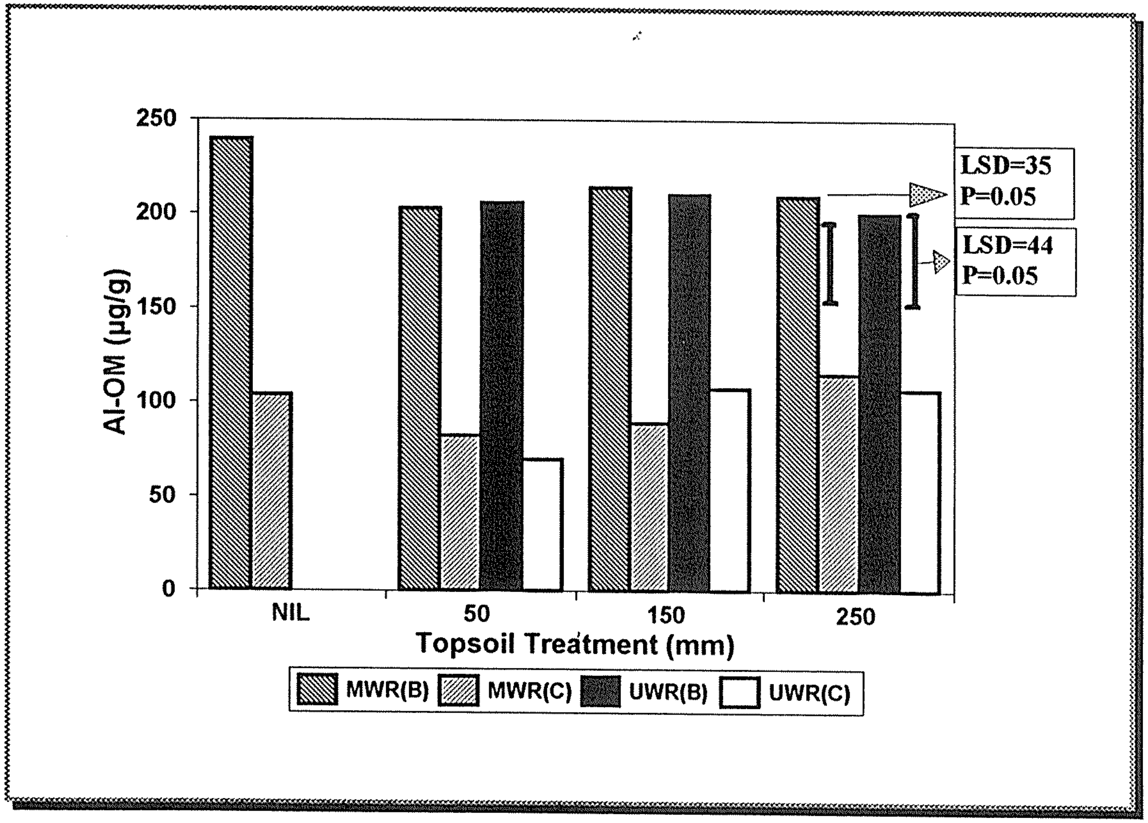


Figure 4.4 Distribution of Al-OM in the unmodified (UWR) and modified (MWR) waste rock interface (B) and at depth (C).

The effect of topsoil, irrespective of liming, had been to provide a reservoir of organic matter (initially, 10.4%, Table 1.1) from which soluble organic ligands could leach into the waste rock interface (B). These organic ligands would have complexed the phytotoxic Al in the waste rock soil solution and made it non-toxic to plants. Such Al-organic matter complexation has been reported by several authors (Foy, 1971; Tan & Binger, 1986; Hern et al., 1988; Shuk-Ching & McColl, 1990). This provides an explanation for similar dry matter yield between the UWR and MWR plots at the end of the three years of trial period even though there was significant difference in the first and the second year (Gregg & Stewart, 1986; 1987). Initially, the soluble organic matter from the topsoil would not have leached in sufficient quantities to complex with phytotoxic Al in the UWR interface (B) and reduce Al toxicity in soil solution. With time, the decomposition and leaching of soluble organic matter would have brought down sufficient organic ligands to complex with Al in the UWR interface (B) and made it non-toxic to plants.

The inverse relationship between Al-Ca and Al-K to Al-OM (Figure 4.5) suggests that as organic matter built up significant fraction of Al was complexed with organic matter, thus reducing Al-Ca and Al-K and increasing Al-OM in the UWR. While liming has largely reduced the Al-Ca and Al-K in the MWR interface (B), they have remained unchanged in the UWR interface (B) - assuming that the Al-Ca and Al-K levels at depth (C) to be the concentrations of these forms in the pre-trial mine waste. The fact that pasture yield was same for MWR and UWR at the end of 3 three years suggests that the Al in UWR soil solution was not toxic to the plants even though the Al-Ca

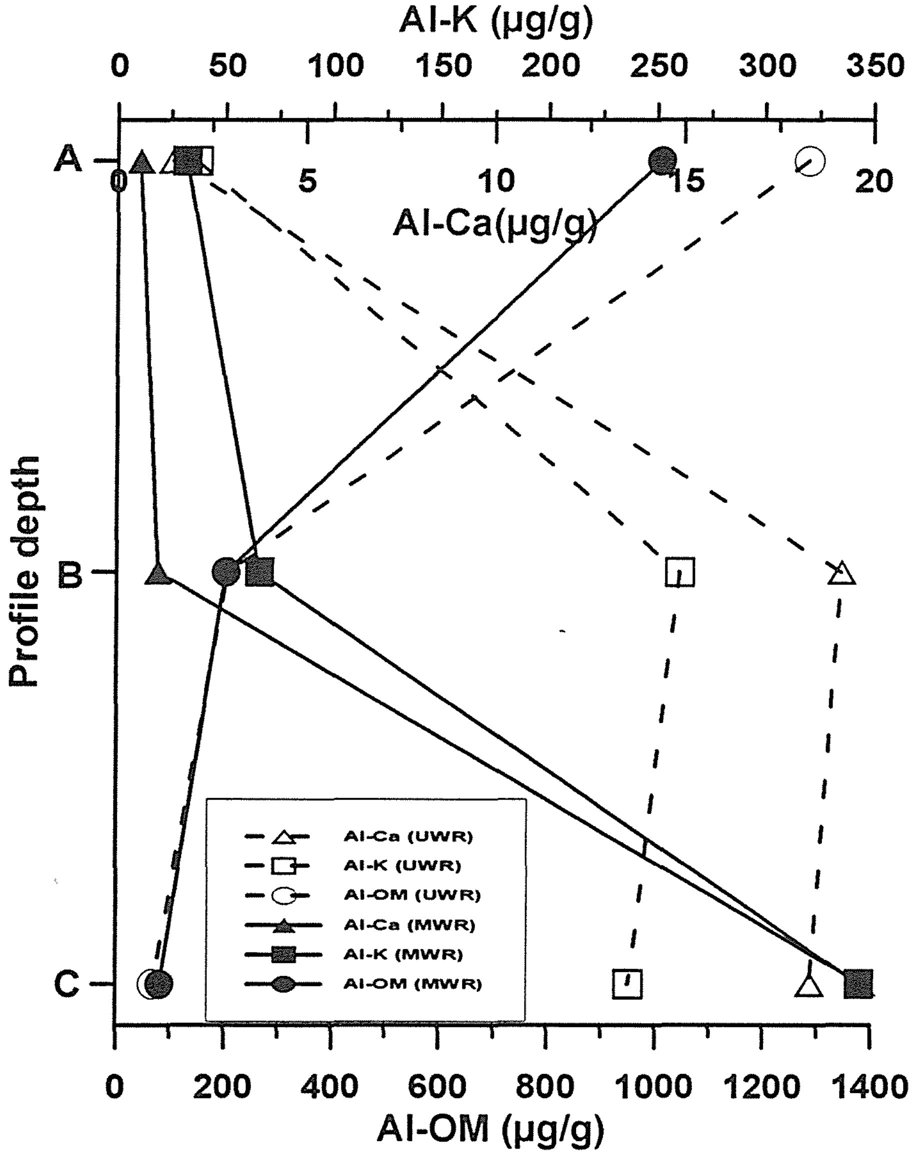


Figure 4.5 Relationship between Al-Ca, Al-K and Al-OM in the MWR and UWR profiles.

and Al-K levels in UWR were much higher than the critical levels suggested in literature (Edmeades et al., 1983; Blamey et al., 1987; Close & Powell, 1989)). Thus it is possible that 0.02 M $CaCl_2$ and 1M KCl-extracts may in fact contain mostly non-toxic forms of Al probably bound to organic ligands (Al-OM) in addition to some plant toxic Al. A study by Percival et al. (1994) have shown that phytotoxic monomeric forms of Al were $< 1\%$ and $< 20\%$ respectively in the 1 M KCl and 0.02 M $CaCl_2$-extracted soil solutions. The rest of the Al were attributed to either polymeric or organic bound, or both. Results of this study support Percival et al's (1994) findings that the currently used 1 M KCl and 0.02 M $CaCl_2$-extracts may not be diagnostic indicators of Al toxicity in plant growth media.

4.1.4. Total Soluble Soil F

The distribution of 0.01 M $CaCl_2$-extractable (total soluble free ion and complexed species) F in the UWR and MWR plots with 50 mm and 150 mm topsoil treatments are given in Table 4.3. The F contents obtained for MWR and UWR (0.3-1.9 $\mu g\ g^{-1}$) were much higher than the values of 0-0.4 $\mu g\ g^{-1}$ reported by Pickering (1985) for surface soils. Study by Larsen & Widdowson (1971) has shown that typical 0.01 M $CaCl_2$ extractable total soluble F was $\leq 0.2\ \mu g\ g^{-1}$ for acid soils. The UWR interface (B) and waste rock at depth (C) had mean F values ranging from 1.5 to 1.9 $\mu g\ g^{-1}$. whereas the MWR interface (B) values ranged from 0.3 to 0.6 $\mu g\ g^{-1}$. The total soluble F in the waste rock at depth (C) has remained at the same level for both UWR and MWR profiles. The topsoil interface F values (A) varied from 1.0 to 1.5 $\mu g\ g^{-1}$ and 0.4-0.5 $\mu g\ g^{-1}$ in the UWR and

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Table 4.3. Distribution of mean total soluble soil F in unmodified (UWR) and modified (MWR) waste rock with topsoil treatments.

0.01M CaCl2-extractable total soluble F, µg/g

F	UNMODIFIED			MODIFIED		
Topsoil, mm	A	B	C	A	B	C
nil	n.d	n.d	n.d	n.d	0.6±0.1	1.2±0.2
50	1.5±0.1	1.8±0.1	1.7±0.0	0.4±0.0	0.4±0.1	1.7±0.1
150	1.0±0.2	1.5±0.1	1.9±0.1	0.5±0.1	0.3±0.0	1.7±0.0

n.d.= Not determined
A = Topsoil interface
B = Waste rock interface
C = Waste rock at depth

MWR plots respectively. The slightly lower value of 1.0 $\mu g\ g^{-1}$ in the 150 mm topsoil treatment of UWR may be due to mixing of topsoil with waste rock below. Lime and fertilizer applications have therefore largely reduced the F in the topsoil interface (A) and MWR interface (B) to $\leq 0.6\ \mu g\ g^{-1}$. The effect of lime on waste rock would have been to reduce the exchangeable Al in the soil solution and precipitating it as Al-hydroxides (Aitken, 1992). Thus there will be insufficient Al available in the soil solution to complex F and keep it in solution (Ares, 1986). Overall, there is no difference in F values between different depths of topsoil treatments.

4.1.5. Al - Fluoride Interactions

The relationship between Al-Ca, Al-K and F in the UWR and MWR profiles is shown in Figure 4.6. Correlation of extractable F data with that of soluble Al-Ca ($r = 0.77$, $n = 22$) and exchangeable Al-K ($r = 0.75$, $n = 22$) showed a significant direct relationship. While the effect of waste rock modification on F, Al-Ca and Al-K is evident in the MWR profile (reduced values at A and B), there is little F variation in the UWR profile (A, B, and C). High levels of F in soil solution can cause Al-F complex formation. Soluble F is one of the most strongly complexing ligands with Al (Pickering, 1985; Ares, 1986). Recent study by Manoharan et al. (1994) have shown that > 90% of inorganic monomeric Al in soil solution is complexed with F in soils treated with phosphatic fertilizers (single super phosphate, North Carolina phosphate rock and diammonium phosphate). MacLean et al. (1992) has shown that F in wheat growth medium effectively reduced Al toxicity. It is possible that a large part of the F from the interfaces (A) and (B) in the UWR

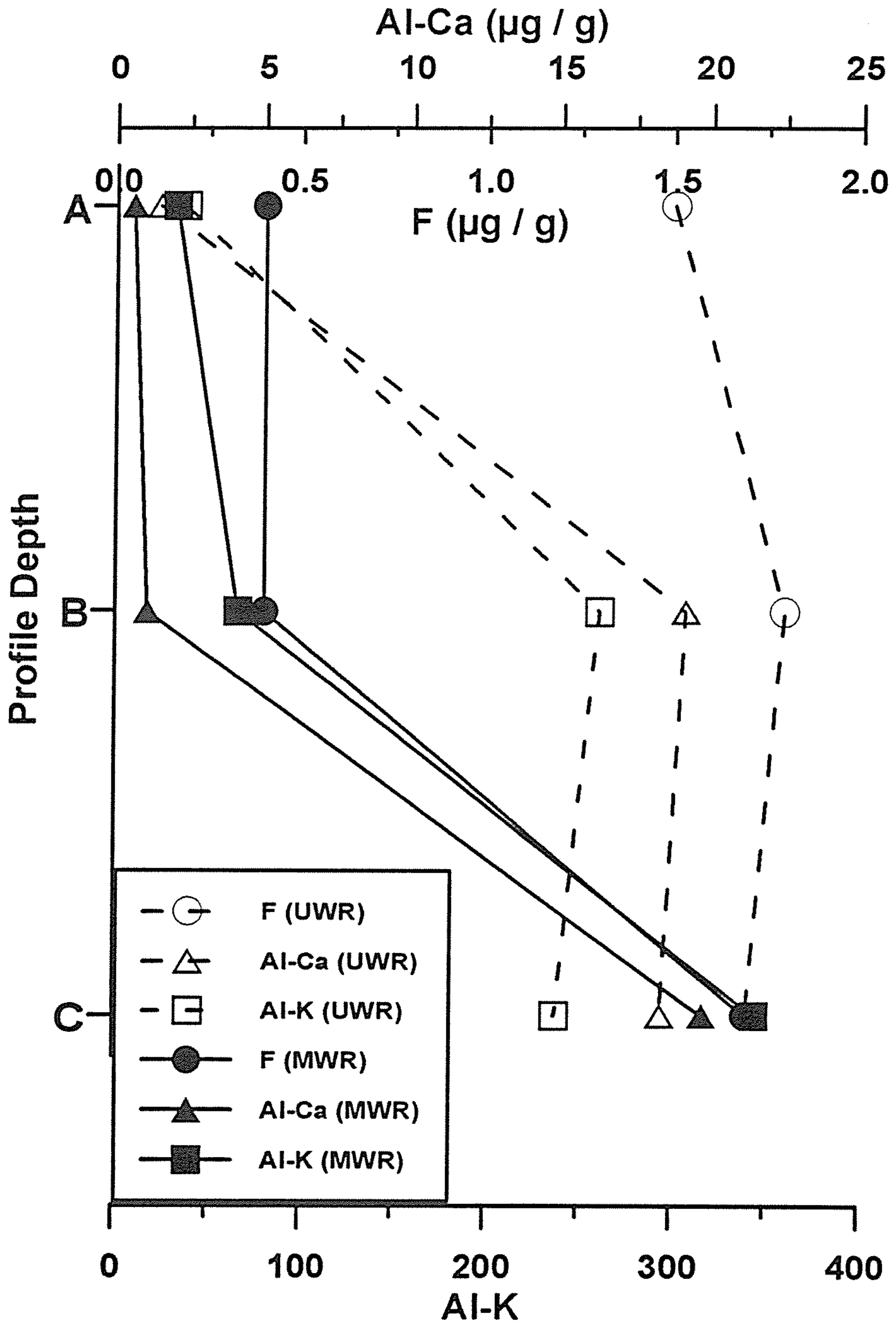

Figure 4.6. Relationship between Al-Ca, Al-K and F in unmodified (UWR) and modified (MWR) profiles.

profile may have complexed with phytotoxic Al and thus reduced Al activity in the soil solution. When F level is high in the soil solution it may readily complex with reactive Al and form non-phytotoxic Al complexes such as AlF^{2+}, AlF_2^+ and AlF_3, depending upon concentrations of other competing anionic ligands. Thus the Al-Ca and Al-K were also likely to contain Al complexed with F amongst other ligands.

In contrast to UWR, in MWR, F as well as Al-Ca and Al-K were low due to the reaction of lime with Al. When lime is added it decreases the Al concentration by formation of $Al(OH)_3$ precipitate. The low concentration of Al reduces the dissolution and desorption of F in the soil and hence low F concentration in soil solution (Munns et al., 1992).

4.1.6 Process of Detoxification of Al

A likely scenario would be that initially the UWR contained toxic levels of Al, restricting root growth, as evidenced from the glasshouse trials on maize and clover and lower dry matter yields obtained from field trial on UWR with topsoil treatments (Gregg & Stewart, 1986; 1987). Liming of the waste rock has raised the pH and increased Ca^{2+} saturation on the exchange complex by displacing Al from the cation exchange sites and precipitating it as non-toxic Al-hydroxides, thus ameliorating Al toxicity. At this stage only limited roots (< 10%) had penetrated the sub-surface waste rock (Gregg & Stewart, 1986). While liming and fertilization of the waste rock facilitated dry matter production by permitting roots to penetrate into the MWR, only topsoil was supporting plant growth on the UWR plots in the initial period of the field trial because the UWR interface (B) was acidic and contained toxic levels of Al. As time prgressed, organic matter decomposed in the topsoil and the organic leachate containing organic ligands entered the UWR interface (B) along with ions such as F^-, SO_4^{2-}, HPO_4^- and SiO_4^+ (B). These organic leachates would have readily complexed a large fraction of the reactive Al and thus reduced its activity in the UWR interface (B) soil solution in the third year of the field trial onwards. Thus in three years time, most of the phytotoxic Al in the UWR soil solution was complexed (with organic ligands and F) into forms non-toxic to plants. Based on the results of this study the following equations are proposed to describe the processes that took place at the UWR and MWR interface (B) towards the end of the field trial period.

MWR : Soil-Al (toxic) + OH^- + Ca^{2+} $\rightleftharpoons$ Soil-Ca^{2+} + $Al(OH)_3$..[1]
UWR : Soil-Al (toxic) + OL + F^- + C $\rightleftharpoons$ Soil-C + Al-OL + AlF..[2]
Where OL = Organic Leachate containing organic ligands.
C = Nutrient Cations.

Phytotoxic Al was thus converted into non-toxic forms of precipitated $Al(OH)_3$ and soluble Al-OL + AlF complexes in the MWR and UWR interfaces (B) respectively of the trial plots. The generally high levels of total exchangeable Al-K and soluble monomeric Al-Ca contained in the UWR would thus include a large fraction of non-toxic Al mobilised by organic and other ligands.

CHAPTER V

5. CONCLUSIONS AND RECOMMENDATIONS

1. A significant, two-fold increase in organic-Al (Al-OM) level after 3 years filed trial at the waste rock interface (B) compared to waste rock at depth (C) indicated that organic ligands from leachates from topsoil have complexed with the phytotoxic Al in the waste rock interface soil solution and made it non-toxic to plant growth. The increase in Al-OM at the waste rock interface (B) was the same irrespective of different depths of topsoil treatments.

2. The relatively high level of soluble F in the unmodified profile show that F may also be responsible for removing phytotoxic forms of Al by forming non-toxic soluble Al-F complexes.

3. The UWR contained high levels of 0.02 M $CaCl_2$-extractable (solution + easily exchangeable) Al-Ca and 1 M KCl-extractable (total exchangeable + solution) Al-K at soil $pH(H_2O) \leq 5.5$ which are thought to be phytotoxic toxic but did not restrict plant growth. This indicated that Al measured by these salts contained mixtures of different forms of Al, only some of which may be toxic to plant growth.

4. Given time and under favourable conditions, direct spreading of minimum depth of topsoil over UWR is sufficient to overcome Al toxicity by providing an organic leachate buffer

which complexes and detoxify labile Al from soil solution. Application of fertilizer containing high amounts of F may also aid in reducing Al toxicity in acid soils.

5. It is recommended that the role of organic matter in ameliorating Al toxicity be further investigated by determining the soluble organic compounds in the various layers of the UWR and MWR profiles. Glasshouse trials on columns of mine waste rock with topsoil as well as other sources of organic matter (e.g:- organic waste) treatments are recommended to further test the effect of organic matter on reducing Al toxicity.

6. Bioassay methods (e.g:- root elongation studies) are recommended to further test the extent of Al phytotoxicity in the UWR and MWR samples from the field trial.

Appendix 1. Selected chemical properties of the waste rock & topsoil from the trial site at Waihi.

Treatment	Depth code	Depth(mm)	pH(H_2O)	pH($CaCl_2$)	Al-Ca(µg/g)	Al-Cu(µg/g)	Al-K(µg/g)	Al-OM(µg/g)	F(µg/g)
MWR	B	30	5.9	5.4	1.8	242	44	198	0.62
MWR	B	30	5.5	5.0	2.1	350	28	322	0.48
MWR	B	40	5.8	5.3	1.8	272	33	239	nd
MWR	B	30	5.8	5.4	2.0	237	39	198	nd
MWD	C	330	5.1	4.1	22.3	450	318	132	1.06
MWD	C	330	5.0	4.0	25.8	478	328	150	1.38
MWD	C	300	5.0	4.1	21.1	379	312	68	nd
MWD	C	350	5.0	4.1	22.6	384	319	66	nd
UWR	B	90	4.9	4.2	22.5	415	298	117	1.72
UWR	B	80	5.0	4.2	19.4	438	231	207	1.82
UWR	B	70	4.8	4.2	19.5	488	249	239	nd
UWR	B	50	5.1	4.4	15.3	528	267	261	nd

MWR = Modified waste rock
MWD = Modified waste rock at depth
UWR = Unmodified waste rock
UWD = Unmodified waste rock at depth
TSU = Topsoil on UWR
TSM = Topsoil on MWR
TS = Undisturbed topsoil (control)
A = Topsoil interface
B = Waste rock interface
C = Waste at depth

pH(H_2O) = 1 : 2.5 (Soil : Deionised water)
pH($CaCl_2$) = 1 : 2.5 (Soil : 0.01 M $CaCl_2$ solution)
Al-Ca = 0.02 M $Cacl_2$-extractable Al
Al-Cu = 0.5 M $CuCl_2$-extractable Al
Al-K = 1 M KCl-extractable Al
Al-OM = Organic-Al, Al-OM = [Al-Cu minus Al-K]
F = 0.01 M $CaCl_2$-extractable total soluble F
n.d = Not determined

Appendix 1............ continued from p. 54

Treatment	Depth code	Depth(mm)	pH(H2O)	pH(CaCl2)	Al-Ca(µg/g)	Al-Cu(µg/g)	Al-K(µg/g)	Al-OM(µg/g)	F(µg/g)
UWD	C	390	5.1	4.1	18.9	358	219	139	1.70
UWD	C	380	5.1	4.3	16.1	312	224	88	1.75
UWD	C	370	5.0	4.1	20.3	245	216	29	nd
UWD	C	350	5.4	4.5	18.1	314	293	22	nd
MWR	B	90	5.8	5.1	0.7	284	59	225	0.50
MWR	B	80	6.8	6.1	1.1	249	50	199	0.29
MWR	B	70	6.4	5.9	1.2	248	54	195	nd
MWR	B	60	5.4	4.6	1.3	293	100	193	nd
MWD	C	390	5.0	4.1	18.5	475	338	137	1.81
MWD	C	380	5.0	4.2	18.4	413	289	124	1.63
MWD	C	370	5.0	4.1	20.7	412	361	51	nd
MWD	C	350	5.1	4.1	21.7	408	392	16	nd
UWR	B	130	4.9	4.2	21.6	670	406	263	1.59
UWR	B	160	4.9	4.2	21.2	591	358	233	1.40
UWR	B	160	5.0	4.2	18.7	430	249	181	nd
UWR	B	180	4.9	4.1	20.5	506	342	164	nd
UWD	C	430	5.2	4.0	21.5	427	365	62	1.82
UWD	C	460	5.1	4.1	21.0	434	306	128	1.90
UWD	C	450	5.1	4.1	20.3	469	338	132	nd
UWD	C	500	5.2	4.3	18.9	437	329	108	nd
MWR	B	150	5.4	4.7	2.0	294	112	183	0.30
MWR	B	160	5.4	4.7	3.1	289	56	233	0.27

Appendix 1............ continued from p. 55

Treatment	Depth code	Depth(mm)	pH(H2O)	pH(CaCl2)	Al-Ca(µg/g)	Al-Cu(µg/g)	Al-K(µg/g)	Al-OM(µg/g)	F(µg/g)
MWR	B	150	6.9	6.5	3.4	282	31	251	nd
MWR	B	180	6.5	6.0	2.4	280	91	190	nd
MWD	C	460	5.2	4.0	21.0	496	382	114	1.70
MWD	C	460	4.8	4.0	20.4	473	389	84	1.75
MWD	C	400	5.1	4.1	20.0	412	332	80	nd
MWD	C	500	5.1	4.1	19.5	451	373	78	nd
UWR	B	260	5.0	4.2	16.5	579	323	256	nd
UWR	B	280	5.0	4.2	17.1	577	296	281	nd
UWR	B	220	4.9	4.2	17.0	505	333	172	nd
UWR	B	280	5.0	4.2	16.3	410	318	92	nd
UWD	C	570	5.1	4.2	16.3	365	294	71	nd
UWD	C	550	5.1	4.2	17.0	380	285	95	nd
UWD	C	550	5.1	4.2	17.5	381	261	120	nd
UWD	C	500	5.1	4.2	16.6	439	298	141	nd
MWR	B	260	6.4	6.0	0.7	254	25	229	nd
MWR	B	280	5.8	5.2	0.8	266	23	244	nd
MWR	B	310	5.2	4.3	0.8	236	34	202	nd
MWR	B	300	6.9	6.4	1.0	222	58	164	nd
MWD	C	560	5.1	4.1	17.3	463	349	115	nd
MWD	C	580	5.2	4.2	17.6	446	355	91	nd
MWD	C	610	5.2	4.2	16.9	369	286	83	nd
MWD	C	550	5.2	4.2	16.6	471	301	170	nd

Appendix 1............ continued from p. 56

Treatment	Depth code	Depth(mm)	pH(H2O)	pH(CaCl2)	Al-Ca(µg/g)	Al-Cu(µg/g)	Al-K(µg/g)	Al-OM(µg/g)	F(µg/g)
TSU	A	60	5.5	5.1	1.3	1462	34	1427	1.43
TSU	A	50	5.4	4.9	1.6	1589	58	1531	1.53
TSU	A	50	5.2	4.9	1.8	1460	22	1438	nd
TSU	A	30	5.5	5.1	1.1	757	33	724	nd
TSM	A	30	5.9	5.4	0.5	1223	42	1181	0.35
TSM	A	50	5.9	5.5	0.5	937	23	914	0.40
TSM	A	30	5.7	5.2	0.6	1127	46	1081	nd
TSM	A	50	5.8	5.4	0.6	869	15	854	nd
TSU	A	100	5.2	4.6	5.4	1274	81	1193	1.15
TSU	A	140	5.1	4.6	6.3	1584	110	1474	0.90
TSU	A	150	5.3	4.6	6.1	1580	106	1474	nd
TSU	A	50	5.6	5.1	6.2	1374	51	1323	nd
TSM	A	110	5.1	4.6	6.1	1685	84	1601	0.51
TSM	A	140	5.2	4.6	5.3	1502	89	1414	0.42
TSM	A	100	5.7	5.2	3.6	1977	20	1957	nd
TSM	A	140	5.3	4.7	4.6	2248	71	2177	nd
TSU	A	250	5.2	4.8	2.2	2138	32	2105	nd
TSU	A	250	5.3	4.8	2.6	2021	42	1979	nd
TSU	A	150	5.3	4.9	1.9	1995	35	1959	nd
TSU	A	250	5.3	4.7	0.8	1296	48	1248	nd
TSM	A	250	5.2	4.7	3.9	1464	70	1394	nd
TSM	A	250	5.2	5.1	4.8	1301	76	1224	nd

Appendix 1............. continued from p.57

Treatment	Depth code	Depth(mm)	pH(H2O)	pH(CaCl2)	Al-Ca(µg/g)	Al-Cu(µg/g)	Al-K(µg/g)	Al-OM(µg/g)	F(µg/g)
TSM	A	250	5.6	5.0	1.7	1116	45	1071	nd
TSM	A	250	5.5	5.0	1.7	1166	50	1116	nd
TS	A	150	5.1	4.9	3.8	1717	40	1677	nd
TS	A	150	5.3	5.2	0.6	1313	67	1246	nd
TS	A	150	5.0	4.8	2.0	1617	42	1576	nd

Appendix 2. Comparison of current analytical data with that of earlier workers. (UWR and MWR profiles with 50 mm and 150 mm topsoil)

Treatment	Depth code	Depth(mm)	pH(H2O)	#pH(H2O)	Al-Cu(µg/g)	#Al-Cu(µg/g)	Al-K(µg/g)	#Al-K(µg/g)
UWR	B	90	4.9	5.1	415	860	298	[378]390
UWR	B	80	5.0	5.0	438	525	231	360
UWR	B	70	4.8	5.0	488	505	249	365
UWR	B	50	5.1	[5.1]5.1	528	515	267	[333]255
UWD	C	390	5.1	[5.0]5.2	358	380	219	300
UWD	C	380	5.1	5.2	312	615	224	224
UWD	C	370	5.0	5.2	245	350	216	300
UWD	C	350	5.4	5.7	314	530	293	145
MWR	B	90	5.8	[7.0]5.8	284	435	59	50
MWR	B	80	6.8	6.7	249	475	50	50
MWR	B	70	6.4	6.3	248	445	54	50
MWR	B	60	5.4	[5.4]5.3	292	310	100	[92]85
MWD	C	390	5.0	5.2	475	375	338	310
MWD	C	380	5.0	5.0	413	425	289	320
MWD	C	370	5.0	5.0	412	425	361	320
MWD	C	350	5.1	5.1	408	455	392	415

UWR = Unmodified waste rock
UWD = Unmodified waste rock at depth
MWR = Modified waste rock
MWD = Modified waste rock at depth
B = Waste rock interface
C = Waste rock at depth

pH(H2O) = 1 : 2.5 (Soil : Deionised water)
Al-Cu = 0.5 M CuCl2-extractable Al
Al-K = 1 M KCl-extractable Al
#= Wright (1991)
[ ]= Gregg & Stewart (1986) - loose data sheet

Appendix 2.....continued from p. 59

Treatment	Depth code	Depth(mm)	pH(H2O)	#pH(H2O)	Al-Cu(µg/g)	#Al-Cu(µg/g)	Al-K(µg/g)	#Al-K(µg/g)
UWR	B	130	4.9	[5.3]5.0	670	665	406	[527]515
UWR	B	160	4.9	4.9	591	645	358	470
UWR	B	160	5.0	5.1	430	555	249	325
UWR	B	180	4.9	4.9	506	625	342	[499]425
UWD	C	430	5.2	5.3	427	480	365	410
UWD	C	460	5.1	5.3	434	440	306	400
UWD	C	450	5.1	5.0	469	505	338	435
UWD	C	500	5.2	[5.1]5.3	436	575	329	350
MWR	B	150	5.4	[6.9]5.5	294	435	112	[83]115
MWR	B	160	5.4	5.5	289	375	56	65
MWR	B	150	6.9	6.8	282	265	31	50
MWR	B	180	6.5	[7.5]6.6	280	350	91	[13]50
MWD	C	460	5.2	5.3	496	490	382	405
MWD	C	460	4.8	4.9	473	460	389	425
MWD	C	400	5.1	5.1	412	435	332	370
MWD	C	500	5.1	5.2	451	575	373	425

Appendix 3. Comparison of 1 M KCl-extractable Al determination by atomic absorbtion spectrophotometry (AAS) and Aluminon methods.

Treatment	Depth code	Depth(mm)	pH(H2O)	*Al-K(µg/g)	Mean *Al-K(µg/g)	#Al-K(µg/g)	Mean #Al-K(µg/g)
MWR	B	30	5.9	44	36±7	28	25±2
MWR	B	30	5.5	28		26	
MWR	B	40	5.8	33		24	
MWR	B	30	5.8	39		23	
MWD	C	330	5.1	318	319±7	337	308±31
MWD	C	330	5.0	328		325	
MWD	C	300	5.0	312		266	
MWD	C	350	5.0	319		302	
UWR	B	90	4.9	298	261±29	272	302±47
UWR	B	80	5.0	231		328	
UWR	B	70	4.8	249		355	
UWR	B	50	5.1	267		255	

MWR = Modified waste rock
MWD = Modified waste rock at depth
UWR = Unmodified waste rock
UWD unmodified waste rock at depth
B = Waste rock interface
C = Waste rock at depth

* Al-K = Al by AAS
\# Al-K = Al by Aluminon method.

Appendix 3.......continued from p. 61

Treatment	Depth code	Depth(mm)	pH(H2O)	*Al-K(µg/g)	Mean *Al-K(µg/g)	#Al-K(µg/g)	Mean #Al-K(µg/g)
UWD	C	390	5.1	219	238±37	267	247±32
UWD	C	380	5.1	224		206	
UWD	C	370	5.0	216		239	
UWD	C	350	5.4	293		277	
MWR	B	90	5.8	59	66±23	40	38±14
MWR	B	80	6.8	50		21	
MWR	B	70	6.4	54		35	
MWR	B	60	5.4	100		55	
UWR	B	260	5.0	323	318±16	298	281±13
UWR	B	280	5.0	296		267	
UWR	B	220	4.9	333		282	
UWR	C	280	5.0	318		278	
UWD	C	570	5.1	294	285±17	314	277±32
UWD	C	550	5.1	285		265	
UWD	C	550	5.1	261		240	
UWD	C	500	5.1	298		290	

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